Enhancement of laser-induced optical breakdown using metal/dendrimer nanocomposites

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We demonstrate that dendrimer nanocomposites (DNC) can be used to remarkably change the laser-induced optical breakdown (LIOB) threshold of a material, owing to a large enhancement of the local electric field. We have implemented LIOB using femtosecond laser pulses in a gold/dendrimer hybrid nanocomposite as a model system. Third-harmonic generation measurements have been employed as a sensitive way for monitoring the LIOB *in situ* and in real time. The observed statistical behavior of the breakdown process is attributed to a laser-driven aggregation of individual DNC particles. The breakdown threshold value of the DNC has been found to be up to two orders of magnitude lower than that of pure dendrimers or normal tissues. [DOI: 10.1063/1.1459483]

Much effort has been devoted to research on laser-induced optical breakdown (LIOB) since the advent of powerful lasers, because of the importance of LIOB in diverse fields including laser surgery, micromachining, three-dimensional optical data storage, solid state physics, etc.[1–3] Recently, in order to obtain an in-depth understanding of the mechanism for LIOB and to find a controllable way for carrying out LIOB, extensive experimental and theoretical investigations have been focused on the laser parameter dependence of the breakdown threshold of optical materials and biological tissues.[4–7] The breakdown threshold, on the other hand, is also determined by the nature of the material itself. So far, much less attention has been paid to altering the breakdown threshold and achieving a controllable breakdown by modifying the material, although LIOB in well-designed materials has a wide range of potential applications. In this study, we demonstrate that one can notably alter the LIOB threshold of a material by incorporating metal nanoparticles, which significantly enhance the electric field localized at their immediate surroundings. We investigated a model system, a gold/dendrimer nanocomposite (DNC), using femtosecond laser pulses. The LIOB threshold of the gold DNC was reduced by up to 113 times in comparison with that of a pure unmodified dendrimer.

Dendrimers are a class of macromolecules possessing a highly branched three-dimensional architecture and well-controlled size, shape and functionality.[8] An amine terminated generation-5 ethylenediamine core poly(amidoamine) (PAMAM) dendrimer was used in this study as a template to form a hybrid nanocomposite.[9] DNCs display unique physical and chemical properties as a consequence of the atomic/molecular level dispersion of the guest(s) with respect to the dendrimer host.[9–11] For the LIOB experiments reported here, a 4.0×10^{-4} M methanol solution of $\{Au(0)_{14}$-PAMAM E5 $\cdot NH_2\}$, which denotes a DNC composed of 14 zero-valent gold atoms per one PAMAM dendrimer (the convention for the notation is given in detail in Ref. 11), was held in a quartz cuvette with 1-mm light path and 1-mm thick wall. The laser system for the LIOB experiment was based on a 250-kHz regeneratively amplified Ti:Sapphire laser.[12] The amplified pulses, with pulse duration of 100 fs and wavelength of 793 nm, were attenuated with a variable neutral density filter, and focused at the front interface between the quartz cuvette and the DNC solution using an f:1 off-axis (60°) parabola. We considered the breakdown at the front interface rather than the rear interface to avoid the complications of spatial and temporal distortion of the pulses caused by self-focusing, group-velocity dispersion, and self-phase modulation when propagating laser pulses through the DNC solution. Some nonlinear optical properties of DNC particles have been studied; a large optical limiting effect in external type silver nanocomposites has been observed, while internal Ag nanocomposites displayed a saturation absorption behavior. The optical limiting was assumed to be due to the formation of microbubbles in the aqueous solution upon absorbing energy from the irradiating laser.[13]

In our experiments, we utilized third-harmonic generation (THG) as a sensitive method for monitoring LIOB in the sample. The THG from the interface was spatially separated from the fundamental transmitted light using a Brewster quartz prism and further filtered with two UV interference band pass filters with center wavelength of 265 nm. The THG signal was monitored during the LIOB process with a photon counting system (Stanford Research Systems, SR400).

Figure 1(a) shows the laser spectrum and the absorption spectra of pure PAMAM and DNC methanol solutions. In contrast to the pure PAMAM dendrimer, the DNC has an absorption maximum around 272 nm, which results from the plasmon resonance of the incorporated gold nanodomains. This absorption peak is close to the one third of the laser wavelength, while there is no absorption in the wavelength regime of fundamental light. The detected intensity of the THG from the interface of DNC methanol solution and

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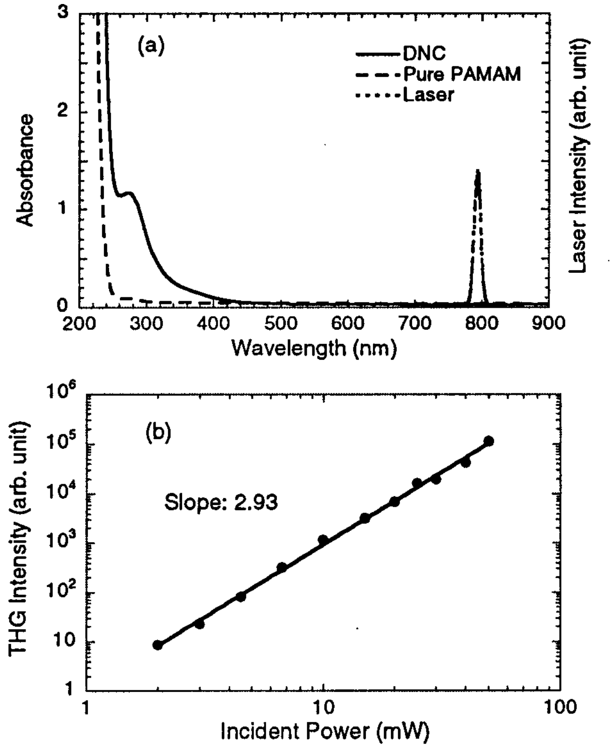

FIG. 1. (a) Absorption spectra of pure PAMAM and DNC in methanol together with laser spectrum. (b) THG intensity from the DNC-quartz interface as a function of the irradiation power. The solid line represents a fit to the experimental data, which has a slope of 2.93, thus confirming the signal is from THG.

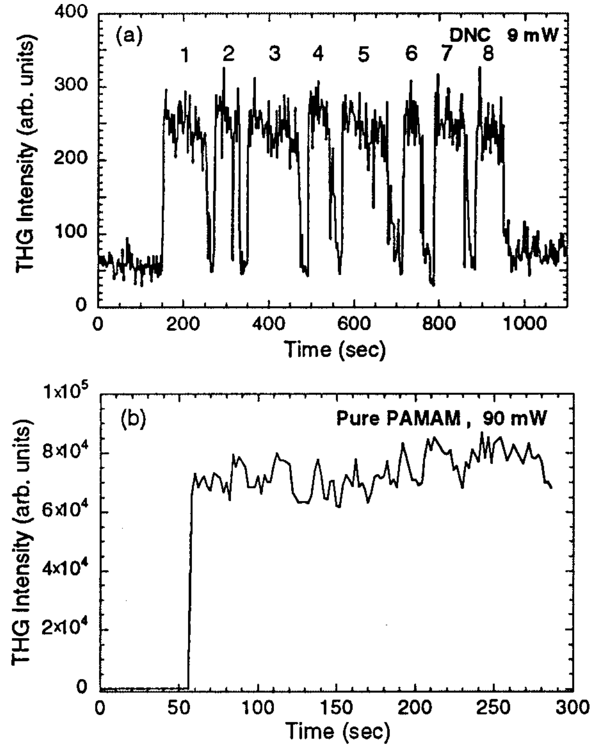

FIG. 2. (a) Change of THG signal during LIOB of DNCs for eight events under laser irradiation of 9 mW. (b) The THG signal from the pure PAMAM-quartz under irradiation of 90 mW. There is no LIOB observed.

quartz surface is plotted as a function of the irradiation power in Fig. 1(b), and a cubic power dependence was verified.

When the laser power was above a certain level, we observed a sudden drop of the THG signal. The variation of THG signal sensitively reflects the change of the material properties, because the intensity of THG is related to the difference of the refractive index or third-order nonlinear susceptibility of the materials on both sides of a laser focus spot at an interface.[14,15] Barad *et al.* employed THG to probe the microscopic structure of transparent samples.[16] Here, we use the THG measurement to monitor the LIOB in the DNC sample. In contrast to conventional criteria for determining breakdown threshold by visual acquisition[4,6] and ablation depth measurement,[5] which is not well defined for the former and not in real time for the latter, the THG measurements provided us with a sensitive way to monitor the LIOB *in situ* and in real time. In addition, because THG is generated only from an interface, we could focus our study on the DNCs adsorbed on or in the vicinity of a surface, since it is known that gold/PAMAM nanocomposites bind to a quartz surface effectively.[16] This system may also serve as a model for DNCs bound to a cell.

As an example, Fig. 2(a) shows eight events of breakdown of the metal/dendrimer nanocomposite sample under irradiation power of 9 mW, where after each breakdown event the sample was shifted to a new position. The rise of the THG signal occurs when a shutter in the laser beam is opened, while the sudden drop of THG indicates the breakdown. In contrast, Fig. 2(b) shows that the THG signal from the interface of the quartz and the pure template PAMAM dendrimer remains unchanged even under much higher irradiation power. We obtained a breakdown threshold of the DNC as low as 0.9 mW, which is corresponding to 9.5 mJ/cm^2 based on a focal spot of 3.5 μm in radius. We carried out a control experiment under the exactly same conditions, and found the breakdown threshold of a pure PAMAM dendrimer (without gold) to be 102 mW (1080 mJ/cm^2), which is 113-fold higher than that of the DNC sample. The breakdown threshold of the DNC is also two orders of magnitude lower than the typical breakdown threshold of a tissue.[7] When irradiating the samples with continuous wave (cw) light instead of 100-fs short laser pulses, we did not observe any breakdown in either DNC or pure PAMAM samples although the cw laser power was above 420 mW. This finding indicates that the observed breakdown of the samples under the ultrashort-pulse irradiation was due to the high peak laser power. This explanation is also consistent with the fact that there is no linear absorption at the laser wavelength [Fig. 1(a)], and thus the possibility for laser-induced thermal breakdown of the sample can be ruled out.

We attribute the remarkable reduction of breakdown threshold of DNC compared with that of pure PAMAM dendrimer to the enhancement of the local electric field by the gold nanodomains in the nanocomposite. As revealed in recent studies,[17–19] metal nanoparticles exhibit strong optical extinction owing to resonantly driven electron plasma oscillations (particle plasmons), which leads to an enhancement of the local light field confined on and close to the surface of the metal nanoparticle. Large enhancement of Raman scattering and fluorescence was previously observed by using metal nanoparticles.[20,21] Our experimental results illustrate that the highly enhanced local field lowers the requirement

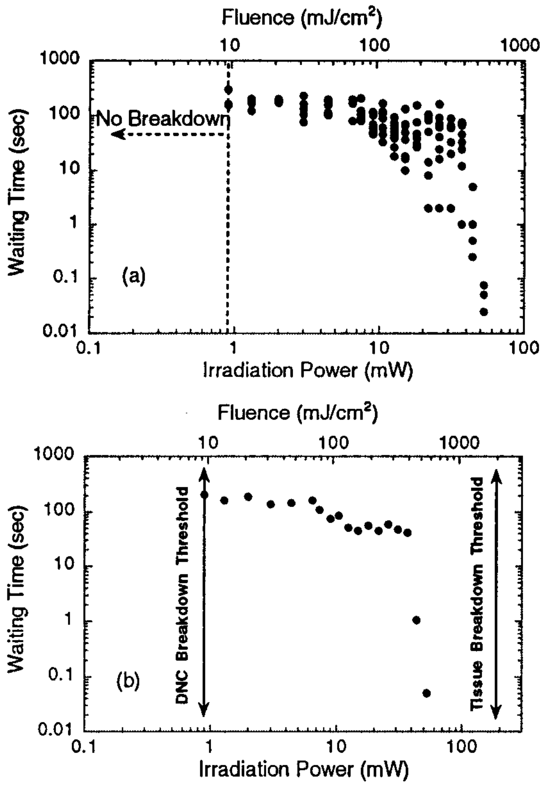

FIG. 3. Laser power and fluence dependence of the waiting time for breakdown of DNC, (a) statistical behavior of the waiting time, and (b) average waiting time. The breakdown thresholds for DNCs and tissues are marked by solid arrows.

for the incident laser power by a factor of more than 100 times to cause a disruptive change to the dendrimer structure. It should be noted here that the plasmon resonance of the DNC used is in the UV region, far away from the laser wavelength. This suggests that aggregation of the DNCs may be necessary in order to form a cluster with a plasmon resonance near the laser frequency. In the experiment, we found that there was a waiting time for the breakdown of DNCs and the waiting time fluctuated in a wide range even under the same irradiation conditions. This statistical behavior of the waiting time and their average values are shown as functions of laser power and fluence in Figs. 3(a) and 3(b), respectively. The existence of the waiting time before breakdown implies that it takes some time for individual DNCs to form aggregates and for the aggregates to grow to a critical size. The aggregation leads to a shift of the plasmon resonance in a local region towards the laser wavelength, thus the field of light is enhanced and eventually to exceed the breakdown threshold. The fluctuation of the waiting time reflects the statistical behavior of the aggregation process. Moreover, we observed that the waiting time becomes notably shorter when the irradiation power is higher than 40 mW, which is still at a power level lower than the breakdown threshold of a pure dendrimer by a factor of 2.5. The sudden decrease of the waiting time implies that there is a change of the breakdown mechanism for the power above 40 mW. However, the details of the breakdown process and the cause of the aggregation are still open questions to be addressed in future studies.

The unique nature of DNC as revealed by this study would open up a wide range of potential applications. The extremely low breakdown threshold would allow one to selectively break down and target DNC molecules to trigger release of encapsulated therapeutics, while avoiding unwanted damage to surrounding tissues. The other potential application is to use DNC to directly break down an organism within a cell (such as a cancer cell) through a nanoheating effect, because the highly enhanced local field of light due to the incorporated metal nanoparticles when irradiated with femtosecond laser pulses is well confined within nanometer region around the DNC. Besides applications in biology and medicine, DNCs may also be used as high-density optical data storage materials owing to their nanometer size and high photosensitivity.

In conclusion, our experiments have demonstrated that the modification of an organic material by incorporating metal nanoparticles to form hybrid nanocomposites significantly reduces the LIOB threshold. A THG measurement was employed to directly monitor the LIOB process. We proposed several intriguing applications by taking advantages of the unique nature of the hybrid nanocomposite particles for biology, medicine, and optical data storage.

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