Rapid Communication

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The role of turbulence in bottom-up nanoparticle synthesis using ultrafast laser filamentation in ethanol

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Abstract: Ultrafast laser filamentation in liquids based on nonlinear optical phenomenon is a new method for bottom-up nanoparticle synthesis. The process is able to synthesize nanomaterials such as nanodiamonds from the liquid precursor. However, the process occurs in a transparent liquid medium and the generation is limited to the interaction volume of the laser beam. In the current work, the effects of turbulence on ultrafast laser filamentation are investigated in an attempt to increase the generation rate. A fixed laser energy, at about ten times the threshold of filamentation in ethanol, is used to ensure persistent filamentation below the vaporization limit. Turbulence in the ethanol precursor was introduced by a high laser repetition rate, mechanical motion, and ultrasonication. The effects were investigated by absorbance measurements of the ethanol sample after laser filamentation, which correlates with the concentration of nanoparticles. For a fixed number of laser pulses, higher absorbance was observed on the sample prepared using a higher repetition rate (53% for 3 kHz compared to 1 kHz). The absorbance of the sample obtained by laser filamentation with cuvette motion increased by ~22% compared to the stationary sample. Finally, when laser synthesis was performed with ultrasonication, the highest increase in absorbance was obtained (~61%). The mechanisms that contributed to the increase are discussed.

Keywords: nanoparticles synthesis, ultrafast laser filamentation, turbulence, ultrafast laser processing

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1 Introduction

Bottom-up synthesis has the advantage of producing nanostructures with fewer defects, a more homogeneous distribution of size and shape, and a simpler process. It is normally obtained in chemical processes, but the progress in laser technology offers an alternate energy source for the synthesis process. Ultrafast laser pulses, especially with the high intense energy pulses in ultrashort duration, interact with solids, liquids, and gases in a unique way to generate various types of nanomaterials. Ultrafast laser filamentation is a process where intense laser pulses self-focus and defocus in a transparent media to form filaments. It is generated by an optical non-linear process that involves the dynamic balance of Kerr self-focusing effect and plasma defocusing [1,2]. It is manifested as a streak of colorful plasma emission during the interaction of an ultrafast laser pulse with transparent media. Laser filamentation has been used for remote sensing [3–5], lightning guiding in air [6], and refractive index modification in solid glass [7,8].

Recent advances show that laser filamentation not only ionizes but also dissociates or recombines molecules, i.e., laser filamentation-induced chemical reaction [9]. An example is the formation of NH molecules from the dissociation of nitrogen and water [10]. Additionally, hydrogenated amorphous carbon was observed during the filamentation of the Ti-sapphire laser in ethylene gas [11]. Our previous study on filamentation also showed that nanodiamonds can be synthesized directly from ethanol without any additives [12,13]. Single-nanometer-sized Au

nanoparticles were obtained from fs laser irradiation of an aqueous mixture of $HAuCl_4$ and n-hexane in aqueous $HAuCl_4$ [14]. The ultrafast laser filamentation process ionizes the medium that acts as a precursor for nanoparticle formation. Such a physical process minimizes the chemical process and is able to produce single-digit nanoparticles.

In our previous study on laser filamentation interaction in ethanol, stronger dissociation of ethanol into carbon species was detected at higher laser energy based on the optical emission spectra and absorbance measurement. However, the process is limited by the localized region of interactions along the filaments. Thus, in the current work, we explore several methods to enhance the yield of the process by introducing turbulence to the liquid medium during the process without direct contact and with an ethanol precursor. The methods are high laser repetition rate, mechanical movement, and ultrasonication.

2 Experimental

A femtosecond laser system (Amplitude Systemes, s-Pulse HP) with a pulse duration of 500 fs at a central wavelength of 1,025 nm was used for nanoparticle synthesis. Ethanol solution (Aldrich, 99.4% purity) was used as a precursor for the synthesis without any additives. As shown in Figure 1, the laser pulses irradiated from the laser were guided by a laser mirror toward a plano-convex lens (f = 50 cm), and the laser beam was focused on the ethanol-containing quartz cuvette (1 cm × 1 cm × 4.5 cm). The ethanol filled up to 3 cm height, and the geometrical focus of the laser pulse was focused 1 cm below the ethanol meniscus.

The laser repetition rate was varied from 0.5 to 3 kHz, while the laser energy was fixed in the range of 460–560 µJ, where laser filamentation occurred readily and consistently. The number of pulses for irradiation was fixed at 1.8 million; thus, the synthesis duration for different repetition rates was 10–30 min. The laser energy was well above the critical power of self-focusing, which was 1.51 MW (0.8 µJ). Subsequently, movement was introduced to the liquid externally (Table 1). A motorized stage was used to move the cuvette during the synthesis along a linear axis back and forth at a speed of 2 cm/s during laser filamentation. The experiment was repeated for laser repetition rates of 1 and 3 kHz. The results are compared with the reference sample that has no motion. In the last experiment, the effect of ultrasonication during the process was studied. The cuvette was positioned at the center of the water-filled ultrasonic cleaner (35 W, 40 kHz). The absorbance of the samples was measured by

Table 1: Experimental conditions for fs laser filamentation in ethanol

Repetition rate (kHz)	Duration (min)	Source of turbulence
1	60	Cuvette not moving
1	60	Moving cuvette at 2 cm/s
3	10	Cuvette not moving
3	10	Moving cuvette 2 cm/s
1	30	No ultrasonication
1	30	With ultrasonication

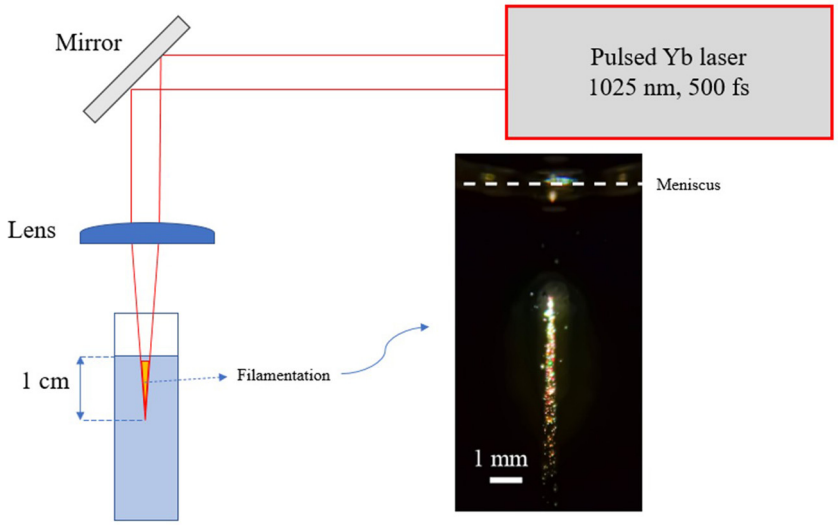

Figure 1: Experiment setup for nanoparticle synthesis using ultrafast laser filamentation (dimension not to scale). The image on the right is the real-time image captured during ultrafast laser filamentation in ethanol. The colorful, bright emissions are filamentation plasma.

using a deuterium-halogen light source and a spectrometer (Avantes 3648, 183–753 nm).

3 Results and discussion

Figure 2 shows the absorbance of the sample subjected to laser filamentation for a fixed laser parameter and the number of laser pulses at repetition rates from 0.5 to 3 kHz. The same peaks were detected for all the samples, indicating that the properties of the sample are the same. The absorbance peak at 228–235 nm was observed, followed by lower intensity peaks at 247, 260, 275, and 300 nm. The peak at 228 nm is the intrinsic absorbance of the diamond (5.4 eV), while 247 nm is attributed to π–π* transition of C═C bonds. The contribution of the absorbance peak at 260 nm is unclear, but the peaks at 275 and 300 nm are due to the n–π* transition of the C═O bond [15,16]. The intensity of the peak increases as the repetition rate increases (Figure 2, inset). The results indicate that more nanoparticles are formed at a higher laser repetition rate. The intensity of the absorbance peak obtained at 3 kHz was 53% higher than that synthesized at 1 kHz. It was also noted that the same spectra (<5% difference) were obtained after 2 weeks. The increase in the intensity of the peaks was also observed consistently if the duration of laser filamentation was increased [13].

Subsequently, the absorbance of samples without and with movements were recorded at laser repetition rates of 1 and 3 kHz. The normalized absorbance of the samples is shown in Figure 3(a) and (b). At the same repetition of 1 kHz, cuvette movement results in a higher change in absorbance. The intensity of the absorbance peak of the ethanol sample synthesized with cuvette movements increased by ~22%. At 3 kHz, the effects of moving the cuvette only increased the absorbance by 4%. The effect was insignificant at a high laser repetition rate. The results show that the movement of the cuvette did not improve much on the synthesis of nanoparticles at 3 kHz. Finally, the liquid motion was introduced during laser filamentation by ultrasonication at a laser repetition rate of 1 kHz. Figure 3(c) shows the normalized absorbance of the samples. The intensity of the absorbance peak increased by 61% when ultrasonication was used. There was no change in absorbance when only ultrasonication was used.

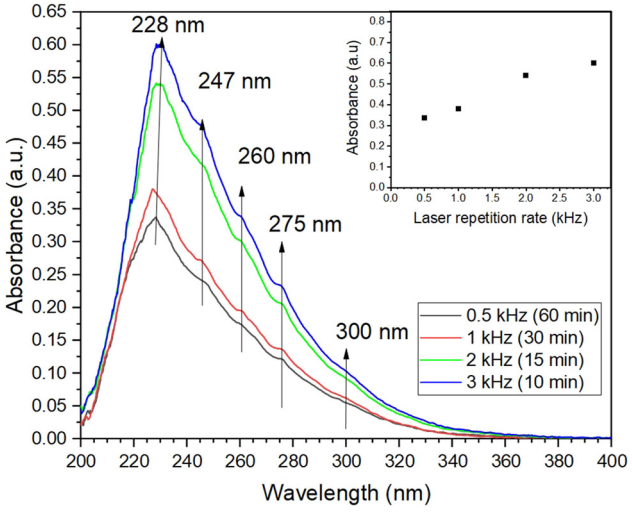

Figure 2: Absorbance of the ethanol sample irradiated for 1.8 million pulses at different repetition rates. The inset shows the increase in intensity of the absorbance peak with laser repetition rate.

During ultrafast laser interaction with ethanol, plasma was produced where ionization occurred in ethanol [13]. As a result, the electrons were accelerated to the surroundings and heated the ethanol because of the temperature gradient induced along the filament. When filamentation occurred in a stationary cuvette, the liquid surrounding the filament was pushed to the sidewall of the cuvette, while the liquid below the filament moved upward to fill up and thus generate a flow that depended on the laser repetition rate. In a separate experiment, the flow was visualized by adding fine carbon powder to ethanol during laser filamentation. The fluid flow trajectory can be traced from the motion of the fine carbon powder (Figure 4). The liquid that was pushed to the sidewall by the filaments proceeded to flow to the lower side of the filament to fill up the region, as reported in another work [17]. This leads to the formation of a circular movement in the region where filamentation occurs.

At a high laser repetition rate, the heat generated is higher [18]. The stronger heat gradient from the interaction zones to the surrounding increased the flow of ethanol to a larger volume. The higher generated heat also increases the rate of the ethanol movement. The ethanol molecules are more energetic because of the induced heat. The carbon powder located at the bottom of the cuvette flows along the flow current in the cuvette and moves upward (Figure 5). At a high repetition rate, the induced flow is able to cover a wider area. The larger coverage of the flow loop and more energetic molecules result in dissociation being more effective.

When filamentation occurs in a stationary cuvette, the movement of ethanol is limited to the region close to the filament. However, when the process was performed with the movement of the cuvette, both the filament position and the pressure gradient in the liquid changed, causing additional movement in the ethanol precursor. The changing flow creates random turbulence on the flow and allows more fresh ethanol outside the flow loop to flow in. As a result, a higher rate of dissociation and also probability for nucleation are obtained.

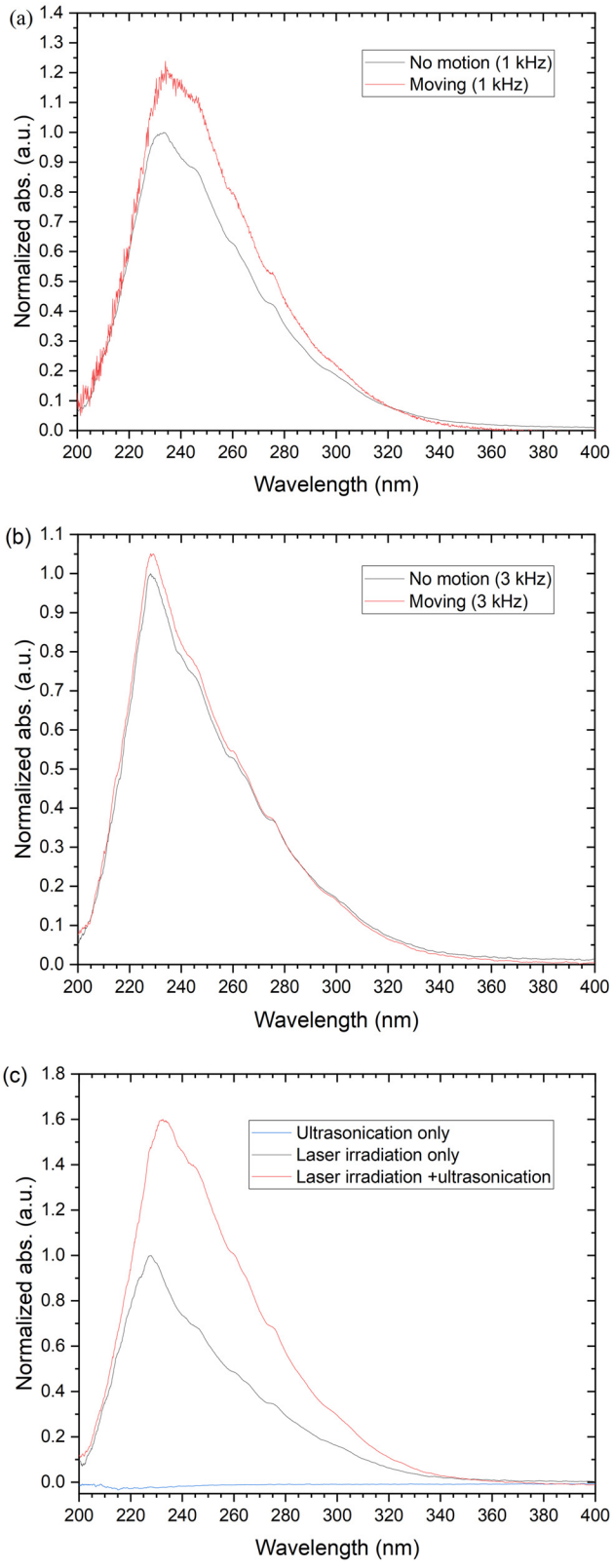

Figure 3: Normalized absorbance of the ethanol sample without and with stage motion at laser repetition rates of 1 kHz (a) and 3 kHz (b). Normalized absorbance of the ethanol sample by only ultrasonication, laser irradiation, and the combination of both at a laser repetition rate of 1 kHz (c).

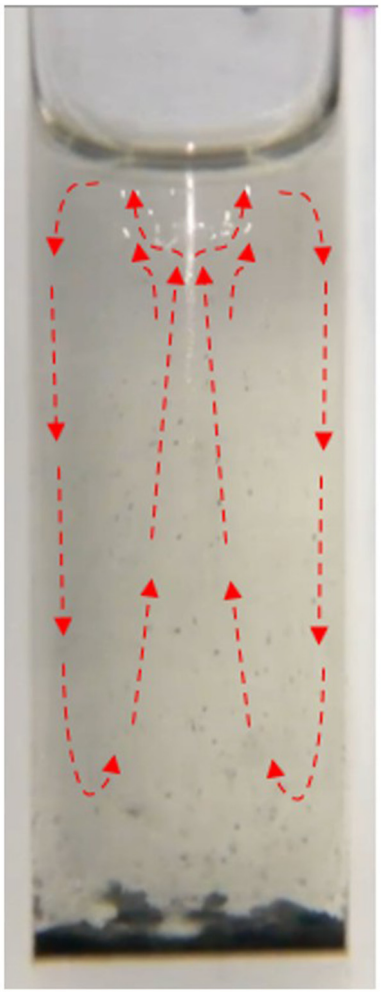

Figure 4: Filamentation in ethanol in the presence of fine carbon powder with the direction of fluid flow indicated by the red arrow.

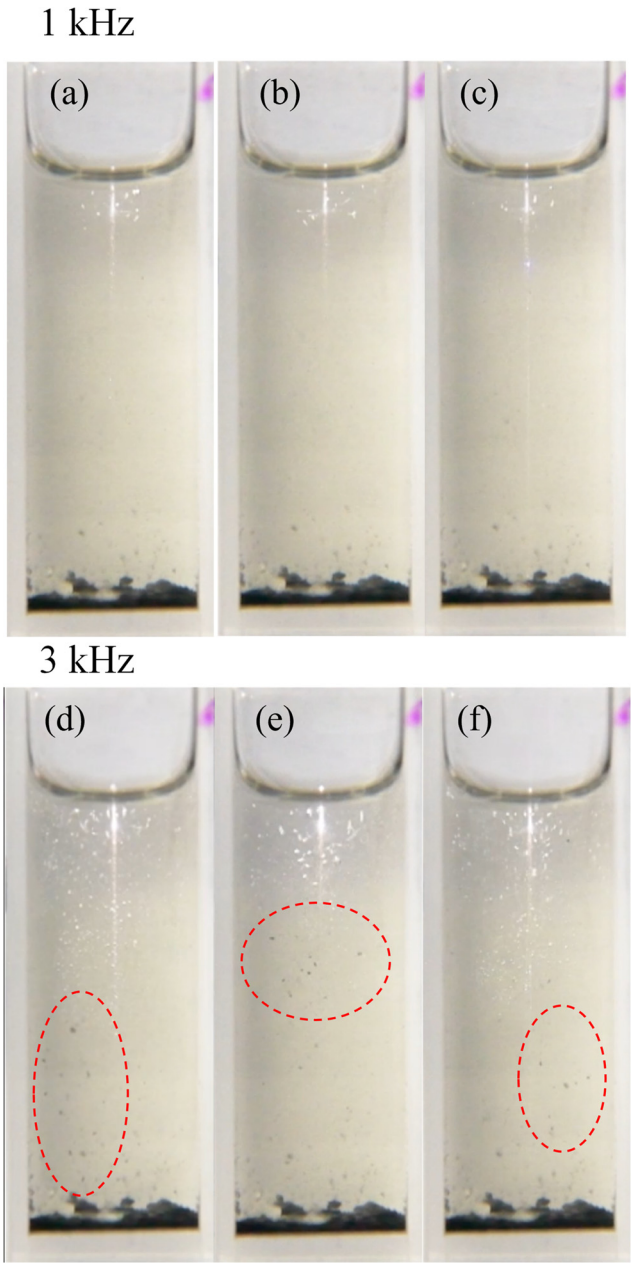

Figure 5: Side view of fine carbon powder motion: (a)–(c) 0, 5, and 10 s of laser irradiation at 1 kHz (stationary); and (d)–(f) 0, 5, and 10 s of laser irradiation at 3 kHz (stationary). The red-dashed circle indicates the carbon powder flowing around.

However, when filamentation in ethanol occurs at a high repetition rate with the movement of the cuvette, there is only a small change in the absorbance. The movement of the cuvette did not increase the absorbance significantly (Figure 3b). The maximum rate of dissociation might have been reached. As the coverage of the flow loop is larger, the size of the cuvette could limit the flow. Finally, ultrasonication vibrates and agitates ethanol at high frequency throughout the volume of ethanol, and thus, the effect is the most significant.

Intrinsically, turbulence in the interaction medium could lower the threshold of multiple filamentations, leading to a higher number of filaments being generated, as observed in air [19]. In another report, turbulence in the medium also enhanced THz generation by multiple chaotically distributed femtosecond filaments in the air [20]. The contribution of this effect is low compared to the improvement in circulation of the precursor molecules because of the nonlinear process. However, it is regenerative as more filaments generate stronger turbulence. As the rate of dissociation also depends on the number of filaments generated, more nanoparticles could be generated with turbulence in addition to the hydrodynamic flow. Based on these results, the use of ultrasonication during ultrafast laser filamentation is the most cost-effective method to increase the yield of nanoparticle synthesis.

4 Conclusion

Ultrafast laser filamentation leads to nanoparticle formation from liquid precursors via an interesting nonlinear optical phenomenon that leads to nanodiamond formation from ethanol. This method can potentially be used to generate single-digit nanoparticles for biomedical applications. The fs laser beam interacts with the liquid precursor for the formation, but the process is limited to the volume of interaction. In an attempt to increase the yield of nanoparticle generation in ultrafast laser filamentation, turbulence is introduced to the process by a higher laser repetition rate, motion of the cuvette container, and ultrasonication. The increase in absorbance, which indicates the higher formation of nanodiamonds, is apparent by using a higher laser repetition rate, although the number of laser pulses is fixed. Next, the sample movement or ultrasonication during the process increases the absorbance. Ultrasonication led to the highest increase in absorbance. The stronger turbulence increases the circulation of the precursor molecules to the interaction zones, thereby contributing to higher absorbance; in addition, turbulence can also promote filamentation and multifilament formation to generate more nanoparticles.

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