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Double-pulse femtosecond laser ablation for synthesis of ultrasmall carbon nanodots

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Abstract

Carbon nanodots (C-dots) with ultrasmall size possessing large surface-to-volume ratio are expected to improve their performance in sensing and catalytic applications. Here, we present a simple strategy to synthesis ultrasmall C-dots using double-pulse femtosecond laser ablation in solution. The size of C-dots reaches minimum value of ~1 nm when the delay between the pulses was approaching the electron-ion relaxation time. In this case, the mean sizes of C-dots in double-pulse ablation are even smaller than that obtained in single-pulse ablation with the same laser fluence due to the suppression of rarefaction wave by the shock wave created by the second pulse. Furthermore, abundant functional groups are created on the surface of C-dots in double-pulse ablation because of reheating the nascent ablated materials by the second pulse. These results demonstrate that the double-pulse technique is therefore an effective strategy beyond single-pulse ablation to synthesis ultrasmall C-dots with abundant surface functional groups as well as other nanoparticle for catalytic and sensing applications.

1. Introduction

Carbon nanodots (C-dots) are a novel carbon-based nanomaterial with size below 10 nm and have attracted tremendous attention due to their unique properties of intense photoluminescence (PL) and high aqueous solubility [1, 2]. C-dots are promising substitutes for the present fluorescent nanomaterials of various applications, such as biological imaging [3, 4], biological and chemical sensing [5–8], catalysis [9, 10], and light-emitting devices [11–13]. For sensing and catalytic applications, it is ideal that C-dots possess ultrasmall size, because it will lead to a dramatic increase in surface-to-volume ratio [14]. This means that a greater number of constituent atoms of C-dots are exposed to their outer environment, which is benefit for improvement of their performance in sensing and catalytic applications. However, it is still a challenge to synthesis C-dots with ultrasmall size using conventional methods such as hydrothermal, microwave-assisted, or chemical oxidation.

As a top-down approach, laser ablation in solution synthesis of C-dots has been attracted great deal of attention because of their significant advantages such as simple, fast, and chemically ‘clean’ [15–18]. Furthermore, the mean size of C-dots synthesized by laser ablation was normally in the range of 2 to 5 nm, which is smaller than that obtained by other methods. Recently, double-pulse ablation (DPA), consisting in the application of two delayed laser pulses, was used to improve the performance of laser-induced periodic surface
structure and laser-induced breakdown spectroscopy [19–22]. Depending on the time delay between the pulses, second pulse can affect the ablation process of first pulse at different stage; finally affect the properties of the obtained product. Previous reports show that DPA is possible to obtain surface structure much smaller than that obtained by single-pulse ablation (SPA) [23, 24]. To be inspired by this result, we investigate the potential of DPA for further reduction the size of obtained C-dots in laser ablation, which is the purpose of this study.

In this paper, we demonstrate that DPA is useful for producing C-dots with a much smaller size than that produced by SPA. Ultrasmall C-dots with mean size of 1 nm were successfully synthesized by double-pulse femtosecond laser ablation in solution. When the delay between the pulses was approaching the electron-ion relaxation time, the mean sizes of C-dots in DPA were even smaller than that obtained in SPA with the same laser fluence due to the suppression of rarefaction wave by the shock wave created by the second pulse. Furthermore, abundant functional groups were created in the surface of C-dots in DPA. The result suggests that DPA promising for synthesis ultrasmall C-dots as well as other nanoparticle for catalytic and sensing applications.

2. Experimental

The experiment reports in this work were performed by focusing two femtosecond laser pulses into graphite powders with size of about 400 nm dispersed in ethanol solution (concentration of 0.02 mg ml$^{-1}$). The experimental setup is shown schematically in figure 1. The femtosecond laser beam from Ti:sapphire laser system (central wavelength: 800 nm, pulse duration: 150 fs, and repetition rate: 1 kHz) was divided into two beams and later recombined into one beam using a set of reflective mirrors and beam splitters. Firstly, the optical lengths of two pulses were adjusted to be equal according to their interference fringe. After that, the optical length of one beam was adjusted by moving its corresponding reflective mirrors, resulting in a wide-range varying of pulse-delay time $\tau_{\text{delay}}$ (0–100 ps). The recombined beam was focused into the suspension by a single lens with focal length of 25 mm (corresponding focus spot size about 4 $\mu$m). The energy of each pulse was controlled by an energy reducer in the corresponding beam path. The laser fluence near the focus of first pulse was set to $F_{\text{single}} = 50$ J cm$^{-2}$ corresponding to an intensity of $3.3 \times 10^{14}$ W cm$^{-2}$. For the second pulse, the fluence near the focus was ranging from 25 to 100 J cm$^{-2}$, corresponds to the value of peak intensity ranging from $1.65 \times 10^{14}$ to $6.6 \times 10^{14}$ W cm$^{-2}$. During the laser irradiation, a magnetic stirrer was used to prevent gravitational settling of the suspended powders. The ablation process was carried out for 30 min for each sample. Centrifugation was used to separate larger carbon nanoparticles and the C-dots were obtained from the supernatant.

Transmission electron microscopy (TEM) images of the C-dots were obtained via a transmission electron microscopy (JEOL JEM 2100) at an accelerating voltage of 200 kV. A small droplet of supernatant containing as-prepared C-dots was deposited on a carbon-coated copper grid and dried by infrared lamp. Normally, the diameters of 700 to 1000 C-dots were measured and the size distribution was obtained. The Fourier transform infrared (FTIR) spectroscopy was performed on a VERTEX 70 (Bruker) using KBr pellet method. A UV-2600 spectrophotometer (Shimadzu) was employed to measure the absorption spectra of the samples.
3. Results and discussion

Firstly, the sizes of C-dots prepared by SPA and DPA are investigated. The TEM images of C-dots prepared by SPA with laser fluence $\text{F}_{\text{single}} = 50 \text{ J cm}^{-2}$ and $2\text{F}_{\text{single}}$; DPA with each pulse fluence of $\text{F}_{\text{single}}$ at $\tau_{\text{delay}} = 2$ and 10 ps are presented in figure 2. The as-prepared C-dots were quasispherical and distributed on the copper grid homogeneously. In the case of SPA, the mean size of C-dots were increased from 1.4 to 2.0 nm when increasing laser fluence from $\text{F}_{\text{single}}$ to $2\text{F}_{\text{single}}$, which is agree well with our previous report on effect of laser fluence on size distribution of C-dots [16]. The mean sizes of C-dots prepared by DPA with $\tau_{\text{delay}} = 2$ and 10 ps were 1.1 and 1.5 nm, respectively. The size of C-dots with $\tau_{\text{delay}} = 2$ ps were ultrasmall with an extremely narrow size range of 0.5 to 2.0 nm, which is important for both fundamental study and practical applications [14].

The sizes of C-dots are strongly dependent on the delay $\tau_{\text{delay}}$ between the laser pulses, as shown in figure 3(a). At short delay ($\tau_{\text{delay}} = 0.5$ ps), the size of C-dots was relatively large and approximated to that obtained in the case of SPA with laser fluence $2\text{F}_{\text{single}}$. The mean size evidently decreased with the increasing of $\tau_{\text{delay}}$ from 0.5 to 2 ps and reached the minimum at $\tau_{\text{delay}} = 2$ ps. When the delay $\tau_{\text{delay}}$ was further increased the size progressively increased and its value at $\tau_{\text{delay}} = 100$ ps was slightly larger than that obtained by SPA with laser fluence $\text{F}_{\text{single}}$. Interestingly, the mean sizes of C-dots prepared at $\tau_{\text{delay}} = 2$ and 5 ps were even smaller than that obtained with SPA at the fluence $\text{F}_{\text{single}}$. The dependency of size of C-dots on the pulse-delay time is similar with the decrease of ablation depth and volume in DPA of bulk target [23, 24]. The result indicates that DPA at
appropriate pulse-delay time can synthesis C-dots with much smaller size compared with that obtained by single pulse.

To further investigate the effect of second pulse on the size of C-dots, DPA at $\tau_{\text{delay}} = 2$ ps with different laser fluence of second pulse was carried out. The laser fluence of first pulse was kept unchanged at $F_{\text{single}}$. The effect of second pulse on the size of C-dots was enhanced with increasing its laser fluence. Indeed, with increasing second-pulse fluence from zero to the fluence of first pulse $F_{\text{single}}$, the size of C-dots gradually decreased (figure 3(b)). The reducing size of C-dots by second pulse reach maximum when the fluence of two pulses were equal. When further increasing second-pulse fluence, however, the size of C-dots obviously increased. At second-pulse fluence $= 2F_{\text{single}}$, the size of C-dots was 2.1 nm, which was slightly larger than that obtained by SPA with $2F_{\text{single}}$. The results demonstrate that the second pulse in DPA affects strongly the ablation process of the first one, subsequently effect the size of obtained C-dots.

The second pulse in DPA not only affects strongly the size but also affects chemical structure of obtained C-dots. All the C-dots prepared by SPA and DPA showed similar category of surface functional groups, as shown in FTIR spectra (figure 4(a)). For example, there are stretching vibrations of O–H bond at 3420 cm$^{-1}$, C–H bond at 2920 cm$^{-1}$, and bending vibrations of C–O bond around 1000–1200 cm$^{-1}$. The main difference among these C-dots was the quantity of these functional groups, which was evident in their UV-visible absorption spectra (figure 4(b)). The absorption spectrum of C-dots obtained by SPA with $2F_{\text{single}}$ was broader and higher compared with that of $F_{\text{single}}$, especially at long wavelength (>275 nm), which corresponding to the absorption
of surface functional groups. Remarkably, the absorption of these functional groups on C-dots were gradually stronger at DPA and reach highest at $\tau_{\text{delay}} = 2$ ps, indicating that more surface functional groups were created at $\tau_{\text{delay}} = 2$ ps. At long pulse-delay $\tau_{\text{delay}} = 100$ ps, however, the absorption weakened. This results demonstrate that DPA is an effective strategy beyond SPA to synthesis C-dots with ultrasmall size and abundant surface functional groups, which is especially benefit for their catalytic and sensing applications.

Physical mechanism for unusual dependency of ablation depth and ablation volume on the pulse-delay in DPA is still under debated [19, 21, 23]. Numerical calculations based on a two-temperature hydrodynamic model suggested that suppression of rarefaction wave by the shock wave created by the second pulse result in the reduction of ablation volume [25]. In this mechanism, both pulses ablate the target simultaneously when the delay is much shorter than electron-ion relaxation time $\tau_{\text{ei}}$. In this case, the ablated volume is approximately equal to that obtained by SPA with double fluence. For $\tau_{\text{delay}} \approx \tau_{\text{ei}}$, the second pulse reheats the nascent ablated materials created by the first pulse resulting in the formation of a shock wave. This shock wave reduces the intensity of the rarefaction wave created by first pulse, subsequently the volume of ablated material decrease.

In laser ablation, C-dots are formed in cavitation bubble created by plasma plume and their size is strongly affected by the concentration of ablated materials [26, 27]. Our previous reports demonstrated that high concentration of ablated materials result in the increase in size of C-dots [6]. Thus, for $\tau_{\text{delay}} \ll \tau_{\text{ei}}$ (several picosecond for graphite [28]), the concentration of ablated materials in DPA are similar with SPA with double fluence and the size of C-dots is approximately equal to that obtained by SPA with double fluence. For $\tau_{\text{delay}} \approx \tau_{\text{ei}}$, the volume of ablated materials decreases due to the reduction of rarefaction wave by the shock wave. Subsequently, the concentration of ablated materials in cavitation bubble decrease and smaller size of C-dots can be obtained. When increasing laser fluence of second pulse, the suppression of ablation by second pulse gradually enhance resulting in the decrease in size of C-dots. However, at high laser-fluence, second pulse can further ablate the target lead to the increase of ablation volume. As a result, the size of C-dots increases. Finally, at long delays $\tau_{\text{delay}} \gg \tau_{\text{ei}}$, the effects of second pulse on ablation process of first one diminish and the size of C-dots gradually increases. In addition, second pulse reheats the nascent ablated materials created by the first pulse generating a high-temperature plasma plume, which result in the dramatically chemical reaction between ablated materials and solution. Therefore, abundant surface functional groups are created on the C-dots in DPA.

4. Conclusions

In summary, C-dots with ultrasmall size and abundant surface functional groups were synthesized by DPA in solution. When $\tau_{\text{delay}} \approx \tau_{\text{ei}}$, the mean sizes of C-dots in DPA was even smaller than that obtained in SPA with the same laser fluence due to the suppression of rarefaction wave by the shock wave created by the second pulse. Meanwhile, the chemical reaction between ablated materials and solution was more dramatic in DPA result in the formation of abundant surface functional groups. The double pulse technique is therefore an effective strategy beyond SPA to synthesis ultrasmall nanoparticle for catalytic and sensing applications.

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