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Photoluminescent carbon nanodots (C-dots) with size tunability and uniformity were fabricated in polyethylene glycol (PEG$_{200N}$) solution using femtosecond laser ablation method. The size distributions and photoluminescence (PL) properties of C-dots are well controlled by adjusting the combined parameters of laser fluence, spot size, and irradiation time. The size reduction efficiency of the C-dots progressively increases with decreasing laser fluence and spot size. The optimal PL spectra are red-shifted and the quantum yields decrease with the increase in C-dots size, which could be attributed to the more complex surface functional groups attached on C-dots induced at higher laser fluence and larger spot size. Moreover, an increase in irradiation time leads to a decrease in size of C-dots, but long-time irradiation will result in the generation of complex functional groups on C-dots, subsequently the PL spectra are red-shifted. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4909506]

I. INTRODUCTION

Photoluminescent carbon nanodots (C-dots) are a new class of carbon nanomaterials that comprise discrete, quasi-spherical nanoparticles (NPs) with sizes below 10 nm.[1] C-dots have attracted great interest due to its low cost, stable photoluminescence (PL), high aqueous solubility, low toxicity, and excellent biocompatibility properties.[1,2] It has been shown that C-dots are excellent material for various applications, particularly for applications in biological labeling, bio-imaging, and drug delivery.[3–5]

The approaches for synthesizing C-dots can be generally classified into two main groups: top-down and bottom-up methods. As a single-step top-down approach, laser ablation in solution (LAS) has recently attracted a great deal of attention.[6–14] LAS is one of the fastest and cheapest method to synthesize a variety of NPs, especially for the metastable phase nanocrystals, such as diamond and related materials.[13–19] Importantly, the significant advantage of LAS over other techniques is chemically "clean" due to its essentially contamination free process and reduced byproduct formation. It is complementary to chemical synthetic methods, in which the presence of residual ions is a serious disadvantage that hinders the applications of NPs.

In the case of high-energy femtosecond laser-induced size reduction in solution, Coulomb explosion model has been proposed to account for the mechanism of the size reduction.[13,20,21] When the femtosecond pulses inject into the solid targets, multiphoton absorption ionization occurs and a plasma plume with high temperature and high pressure is formed. Under these extreme conditions, NPs with size of several nanometers can be produced through Coulomb explosion induced size reduction.[20] Meanwhile, the surface

functionalization on NPs takes place simultaneously with the formation of NPs.[6] In the Coulomb explosion process, the properties of the focusing conditions of the laser pulses and the solutions can greatly influence the thermodynamic and kinetic properties of the evolution of the plasma plume,[22,23] and finally affect the sizes and structures of NPs.[14,24,25] In the previous reports, effect of the laser parameters on the size reduction efficiency of LAS induced noble metal and semiconductor NPs has been studied.[19,23,26,27] However, the influence of laser parameters on the size reduction of C-dots, especially the effect on the PL properties of produced C-dots has not been reported.

In this paper, starting with graphite powder of about 400 nm in diameter, we discuss the effect of laser fluence, spot size, and irradiation time on C-dots prepared by femtosecond laser-induced size reduction in polyethylene glycol (PEG$_{200N}$) solution. As a result, size reduction efficiency and PL properties of C-dots can be controlled by changing laser fluence, spot size, and irradiation time. The results suggest that this strategy could be a simple and general way to prepare C-dots with tunable size and PL properties.

II. EXPERIMENT

In a typical procedure, 20 mg of initial carbon powder with a mean size of 400 nm was dispersed into 50 ml of PEG$_{200N}$. After ultrasonication, about 10 ml of suspension was put into a glass beaker (outside diameter × height: 25 mm × 35 mm) for laser irradiation. A Ti: sapphire femtosecond laser system with central wavelength of 800 nm, pulse duration of 150 fs, and repetition rate of 1 kHz was used. Laser beam was focused into the suspension by lens with different focal lengths, i.e., 25 mm, 50 mm, and 100 mm (corresponding focus spot size about 4 μm, 8 μm, and 16 μm, respectively), respectively. During laser irradiation, a

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magnetic stirrer was used to prevent gravitational settling of the initial powders. After laser irradiation, the solution was centrifuged to separate larger carbon particles and C-dots. C-dots can be obtained in the supernatant.

A high resolution transmission electron microscopy (HRTEM, model JEM-ARM200F) was used to record transmission electron microscopy (TEM) and HRTEM images of the C-dots. 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 500 to 1000 C-dots were measured and the size distribution was obtained. U-3010 spectrophotometer (Hitachi) was employed to measure the absorption spectra of samples. The Fourier transform infrared spectroscopy (FTIR) was performed on VERTEX 70 (Bruker). The PL spectrum measurements were done on the Fluoromax-4 spectrometer (Horiba Jobin Yvon). The quantum yields of C-dots were measured by comparing the integrated photoluminescence intensities and the absorbency values of the samples with the reference quinine sulfate in 0.1 M H_2SO_4.

III. RESULTS AND DISCUSSION

A. Effect of laser fluence

Firstly, we investigated the effect of laser fluence on the produced C-dots size and PL properties. The laser pulses were focused into the carbon powder suspension at different laser fluences ranging from 150 J/cm^2 to 1000 J/cm^2, while all other parameters were kept constant. The irradiations were performed during 3 h for each sample. Figs. 1(a)–1(c) show the TEM images of C-dots prepared with spot size of 8 μm at laser fluences of (a) 150 J/cm^2, (b) 350 J/cm^2, and (c) 750 J/cm^2, respectively. The as-prepared C-dots distribute on the copper grid homogeneously and no large aggregation can be observed, indicating that the C-dots are well dispersed in solution. The selected area electron diffraction (SAED) patterns of C-dots prepared at laser fluence of 750 J/cm^2 are shown in Fig. 1(d). The ratio of squares of the diffraction ring radius is 3:8:11:16, which indicates that the as-prepared C-dots have a diamond-like structure, and the rings correspond to the {111} {220} {311} {400} planes of a diamond structure.[14,28] The HRTEM images of C-dots prepared at laser fluences of 150 J/cm^2 and 750 J/cm^2 in Figs. 1(e) and 1(f) exhibit obvious crystal lattices with the same lattice spacing of 0.21 nm, which is nearly the same as that of {111} planes of cubic diamond.

The size distributions of corresponding products in Figs. 1(a)–1(c) are presented in Figs. 1(g)–1(i), respectively. The size distributions of as-prepared C-dots are in a narrow range of about 1–4 nm. The maximum values of the fitted Gaussian peak for three products are 1.5, 1.7, and 2.5 nm, respectively. The corresponding size distributions of C-dots are extended from C-dots prepared at laser fluences of 150 J/cm^2, 350 J/cm^2 to 750 J/cm^2. Furthermore, the size distributions of C-dots, especially C-dots prepared at laser fluence of 150 J/cm^2, are narrower in comparison with that of previous reports.[5,6,29]

Fig. 2 summarizes the effect of laser fluence on the mean size of the C-dots produced with different spot sizes of
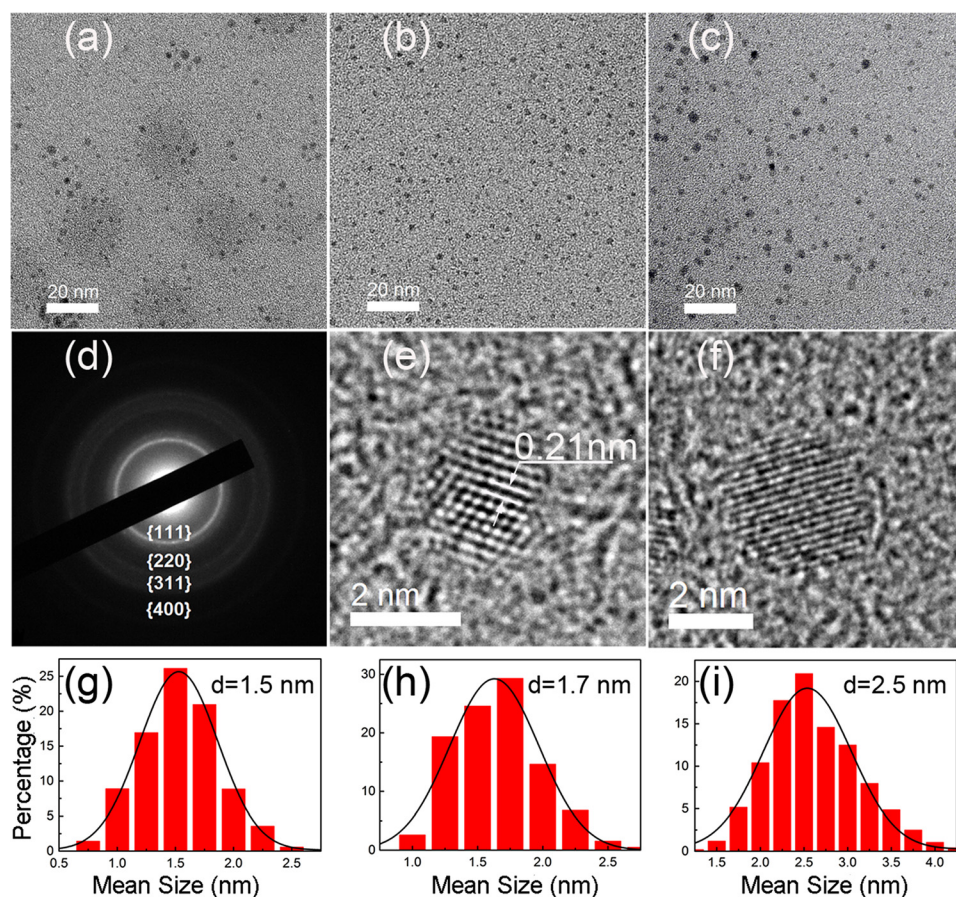
FIG. 1. TEM images of C-dots prepared by femtosecond laser irradiation for 3 h with spot size of 8 μm at laser fluences of (a) 150 J/cm^2, (b) 350 J/cm^2, and (c) 750 J/cm^2. (d) The SAED patterns of C-dots obtained at laser fluence of 750 J/cm^2. Typical HRTEM images of C-dots prepared at laser fluences of (e) 150 J/cm^2 and (f) 750 J/cm^2. The corresponding size distributions of C-dots prepared at laser fluences of (g) 150 J/cm^2, (h) 350 J/cm^2, and (i) 750 J/cm^2.
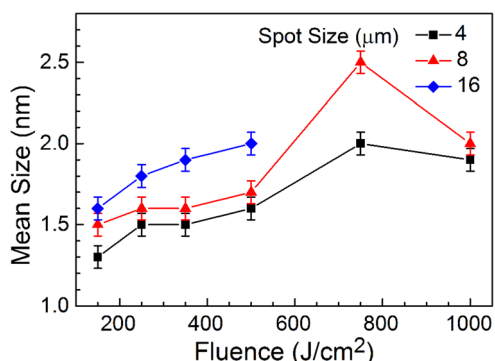
FIG. 2. The dependence of the mean size of as-prepared C-dots on the laser fluence with different spot sizes: 4 μm (black squares), 8 μm (red triangles), and 16 μm (blue diamonds).

4 μm, 8 μm, and 16 μm, respectively. The inspection of Fig. 2 reveals that the mean sizes of the C-dots are laser fluence-dependent: the mean size progressively increased when the laser fluence was from 150 J/cm^2 to 750 J/cm^2 and decreased at high laser fluence of 1000 J/cm^2. The results suggest that laser fluence strongly affects the sizes and size distributions of C-dots.

Here, we give a brief interpretation on the possible mechanism of effects of laser fluence on C-dots in femtosecond laser-induced size reduction in solution. To rule out the possibility of formation C-dots from the carbonization of PEG$_{200N}$ during the femtosecond laser irradiation process, a blank experiment was conducted and the results show no evidence of existence of C-dots in the TEM images and PL study, indicating that the C-dots originate from laser ablation of graphite powder. As suggested by several researchers, when the femtosecond pulses inject into the solid targets, Coulomb explosion takes place and a plasma plume with high temperature and high pressure is formed due to multi-photon absorption ionization. When the plasma plume expands and cools down, a cavitation bubble is generated in solution. With the expansion of the bubble, the carbon nanoclusters with high surface energy in cavitation bubble tend to aggregate into larger NPs.[22,25,30] When the temperature decreases and internal pressure of the bubble drops to a value lower than in the surrounding solution, the C-dots with reduced size are formed.[23] Previous reports on LAS showed that the shorter lifetime of the cavitation bubble, causing faster quenching rate, is proposed to be the reason for more efficiently reduced NPs size and more surface defects of NPs.[22]

In this work, with the increase in laser fluence from 150 J/cm^2 to 750 J/cm^2, the temperature and pressure of the plasma plume increase, resulting in the increase in bubble size and lifetime. As a result, the larger sizes of C-dots are produced in the cavitation bubble by aggregations of nanoclusters. However, when the laser fluence is further increased, the ablation efficiency of C-dots increases significantly. In the same irradiation time, a large number of already-size-reduced C-dots will be further ablated repeatedly, and smaller C-dots will be produced. This explains why the size of C-dots prepared at laser fluence of 1000 J/cm^2 was smaller than that of C-dots prepared at laser fluence of 750 J/cm^2.

To further study the effect of laser fluence on its structures, we explore the UV-Vis absorption spectra and FTIR spectra of C-dots prepared with spot size of 8 μm at laser fluences of 150 J/cm^2, 350 J/cm^2, and 750 J/cm^2, respectively. The UV-Vis absorption spectra of three C-dots show the same absorption peaks at 205 nm and 260 nm, which are attributed to the π-π* transition of C=C bond from carbogenic core (Fig. 3(a)).[31,32] The absorption spectrum of C-dots prepared at laser fluence of 750 J/cm^2 is obviously broader and higher than that of the other two samples, which can be attributed to the existence of more surface functional groups on its surface.[33] The characteristic absorption bands of surface functional groups in these C-dots can be detected by FTIR spectra (Fig. 3(b)). The FTIR spectra show that most surface functional groups in three C-dots are similar to each other. For example, there are stretching vibrations of O-H at 3420 cm^{-1},[34] C-H at 2920, and 2855 cm^{-1},[14] vibrations of C=O at 1630 cm^{-1},[34] bending vibration of CH$_2$ at 1350–1460 cm^{-1},[35] and vibration of C-O around 1000–1200 cm^{-1}.[14] The main difference among these C-dots is the quantity of these functional groups. The quantity in C-dots prepared at laser fluence of 750 J/cm^2, especially hydroxyl group, is obviously larger compared with that in the other two samples. The results indicate that more surface functional groups were created with the increase in laser fluence.

Figures 4(a)–4(c) show the emission spectra of C-dots prepared with spot size of 8 μm at laser fluences of 150 J/cm^2, 350 J/cm^2, and 750 J/cm^2, respectively. The emission of C-dots prepared at laser fluence of 150 J/cm^2 is mainly in the

FIG. 3. (a) The UV-Vis absorption spectra and (b) the FTIR spectra of C-dots prepared with spot size of 8 μm at laser fluences of 150 J/cm^2, 350 J/cm^2, and 750 J/cm^2.
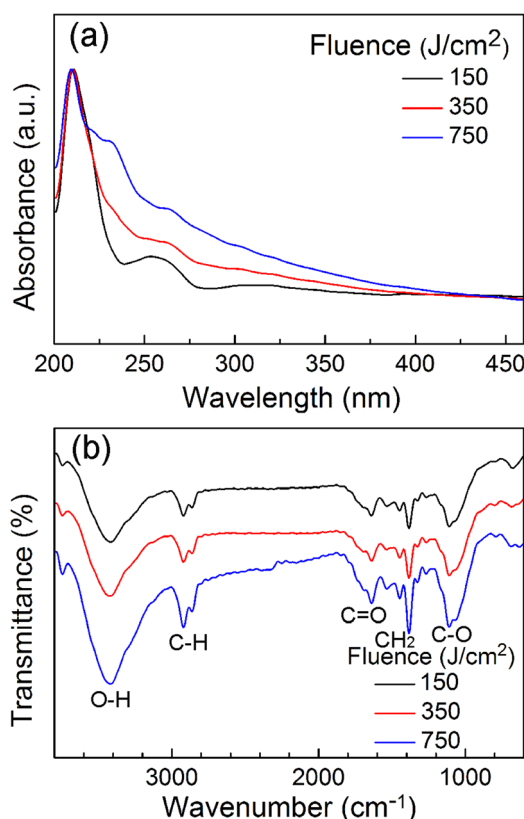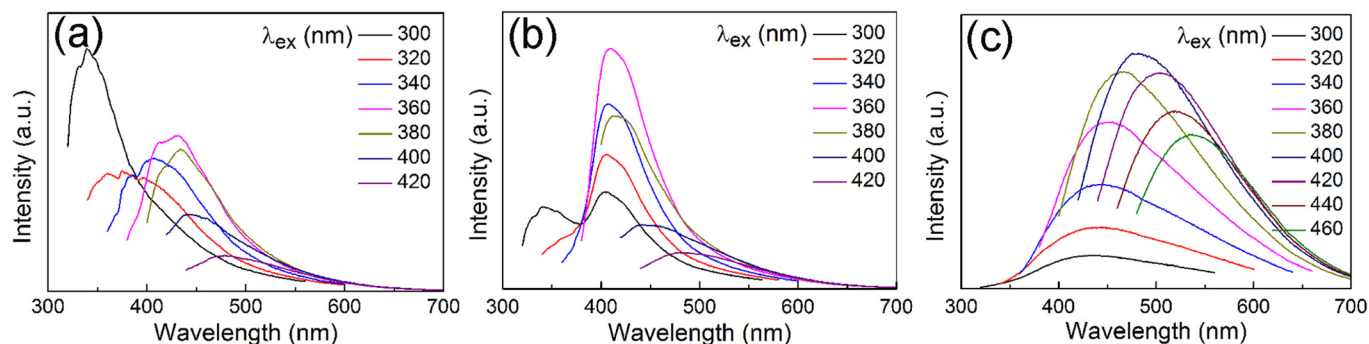
FIG. 4. Emission spectra of C-dots prepared with spot size of 8 μm at laser fluences of (a) 150 J/cm^2, (b) 350 J/cm^2, and (c) 750 J/cm^2.

UV region with the maximum intensity around 340 nm at an excitation wavelength of 300 nm. The C-dots prepared at laser fluence of 350 J/cm^2 showed a maximum emission at 410 nm with 320 nm excitation, while those prepared at 750 J/cm^2 showed a maximum emission at 480 nm with 400 nm excitation. From the PL spectra, we can see that optimal PL emission of C-dots was red-shifted with increasing the laser fluence. Furthermore, the PL spectra of C-dots prepared at laser fluence of 750 J/cm^2 are broader and smoother than those of the other two samples. The quantum yields of the three samples at corresponding optimal emission peak were also measured. Quantum yields of C-dots prepared at laser fluence of 150 J/cm^2, 350 J/cm^2, and 750 J/cm^2 are estimated to be 13.6%, 6.2%, and 3.4%, respectively. It indicates that smaller C-dots which prepared at lower laser fluence exhibit stronger PL emission. It should be noted that although the PL emission of C-dots can be very strong even after several months, they exhibit red-shifted after irradiation of UV light for several hours (desk UV lamp, 365 nm). This result could be attributed to the increase in carbonyl groups originated from photochemical oxidation, which is similar with previous report of other researcher.[36]

There are some suggestions about the luminescence mechanism of C-dots, such as quantum-confinement effects, emissive traps, electronic conjugate structures, etc.[37] Recent reports suggested that drastic competition among different emission centers (special structure consisting of edge carbon atoms and functional groups) and traps dominates the optical properties of C-dots.[35] In this mechanism, all of the surface functional groups may become different competition channels, including radiative and nonradiative processes. Hence, more unitary functional group with larger quantity on C-dots will result in higher PL quantum yield. In contrast, the PL spectra are more red-shifted and lower quantum yield can be observed at C-dots with complex surface functional groups.[33,35]

In this study, with the increase in laser fluence, the chemical reactions between the nanoclusters and the solution molecules are more drastic and prolonged due to higher temperature of the plasma plume. Consequently, more different relaxation channels are created by surface functional groups which are more out of control with the increase in laser fluence. As a result, the PL spectra of C-dots prepared at laser fluence of 750 J/cm^2 are broader, red-shifted and with lower quantum yield compared with that of C-dots prepared at laser fluences of 150 J/cm^2 and 350 J/cm^2. Our results suggest that

a decrease in laser fluence in laser-induced size reduction leads to the blue-shift of PL spectra and the increase in quantum yield.

B. Effect of spot size

In order to observe the effect of spot size on the C-dots, we performed a series of experiments where the spot size was varied while keeping other parameter constant. The spot sizes were 4 μm, 8 μm, and 16 μm in diameter. The irradiations were carried out with laser fluences of 150 J/cm^2, 250 J/cm^2, and 500 J/cm^2 for 3 h. Fig. 5(a) shows the mean size of the as-prepared C-dots as a function of the laser spots size at fluence of 150 J/cm^2, 250 J/cm^2, and 500 J/cm^2, respectively. From the figure, we can see that the mean size increased almost linearly with increasing the spot size. For example, the mean sizes of C-dots prepared at laser fluence of 250 J/cm^2 with spot size of 4 μm, 8 μm and 16 μm were measured to be 1.5 nm, 1.6 nm, and 1.8 nm, respectively. In the LAS process, a larger spot size will induce a smoother gradient of temperature and pressure at the irradiation area. Consequently, it will cost a longer time for the cavitation bubble to decrease its temperature and drops internal pressure to a value lower than in the surrounding solution. The life time of cavitation bubble is prolonged, and C-dots with larger mean size are produced as discussed in Sec. III A.

Fig. 5(b) shows the corresponding optimal emissions of C-dots prepared with different spot sizes at laser fluence of 250 J/cm^2. The PL spectra are red-shifted and broader with the increase in spot size, being similar with results shown in Sec. III A which can be explained by the generation of more surface functional groups on C-dots. With the increase in spot size, more functional groups can be attached on C-dots through chemical interactions between the nanoclusters and the solution molecules during long-time growth of nanoclusters in the bubble. Then, the PL spectra are red-shifted and broader when spot size increases.

C. Effect of irradiation time

In this experiment, the total irradiation time was varied from 2 to 4 h, while the spot size in this study was about 16 μm and the laser fluence was kept at 150 J/cm^2. We observed that with increasing the irradiation time, the size of as-prepared C-dots became smaller and size distribution was narrower. The solid squares in Fig. 6 show the dependence
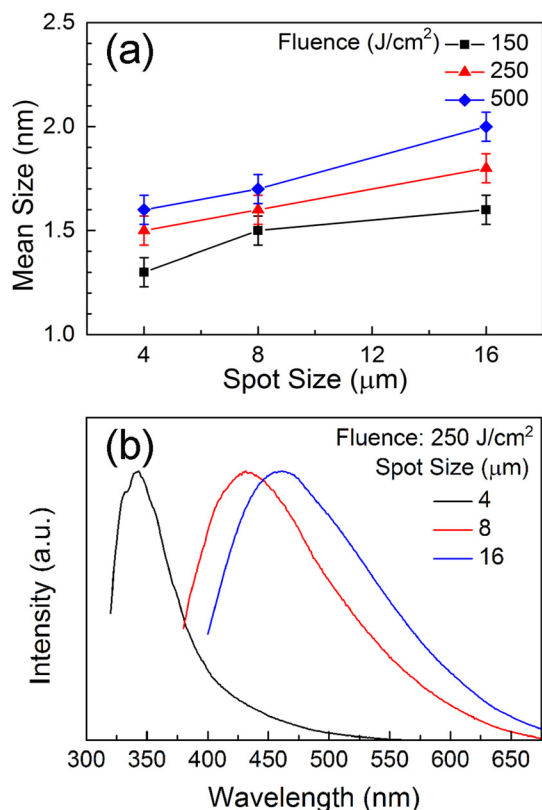
FIG. 5. (a) Plot of mean size of C-dots as a function of spot size at three different laser fluences: 150 J/cm^2 (black squares), 250 J/cm^2 (red triangles), and 500 J/cm^2 (blue diamonds). (b) The optimal emission spectra of C-dots prepared at laser fluence of 250 J/cm^2 with spot size of 4 μm (black curve), 8 μm (red curve), and 16 μm (blue curve).

have more surface functional groups than initial ones. The more surface states are created in the C-dots, resulting in a red-shifted emission. The results suggest that increase irradiation time is a simple way to prepare ultra-small C-dots with long wavelength emission spectra.

IV. CONCLUSION

We have discussed the effect of laser fluence, spot size, and irradiation time on C-dots prepared by femtosecond laser-induced size reduction in PEG$_{200N}$ solution. The size distributions and PL properties of C-dots can be well controlled by adjusting the combined parameters of laser fluence, spot size, and irradiation time. The mean size progressively decreases with decreasing laser fluence and spot size, and the corresponding PL spectra are narrower, blue-shifted and higher quantum yield due to more unitary surface functional group is created. Moreover, the effect of irradiation time reveals that an increase in irradiation time leads to a decrease in size of C-dots, but long irradiation time will result in the generation of many categories of functional groups on C-dots, subsequently the PL spectra are red-shifted. The results of this work reveal that controlling the combined laser parameters in femtosecond laser-induced size reduction in solution could be a simple and general way to prepare C-dots with tunable size and PL properties as well as other NPs with unusual structures.

of the mean size of as-prepared C-dots as a function of the irradiation time. The mean size decreased from 2.1 nm to 1.3 nm when the irradiation time increased from 2 to 4 h. The triangles in the figure show the optimal PL emission wavelength of corresponding as-prepared C-dots. What is unexpected is that the optimal PL emission was red-shifted with decreasing the size, being against with the results given above. It is speculated that some already-size-reduced C-dots will be further ablated in the LAS process when the irradiation time is extended. As a result, the size of C-dots is further reduced, and chemical reactions between the C-dots and solution molecules take place again. Therefore, smaller C-dots
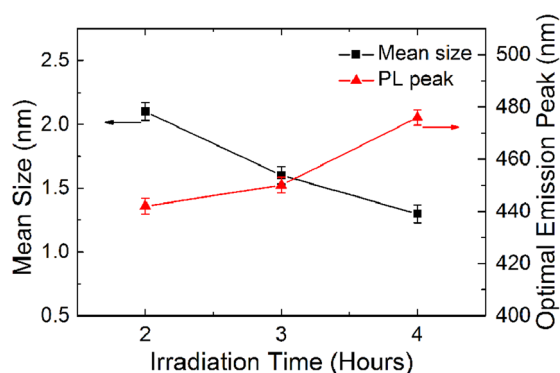

FIG. 6. The mean size (black squares) and corresponding optimal emission peak (red triangles) of as-prepared C-dots versus irradiation time.

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