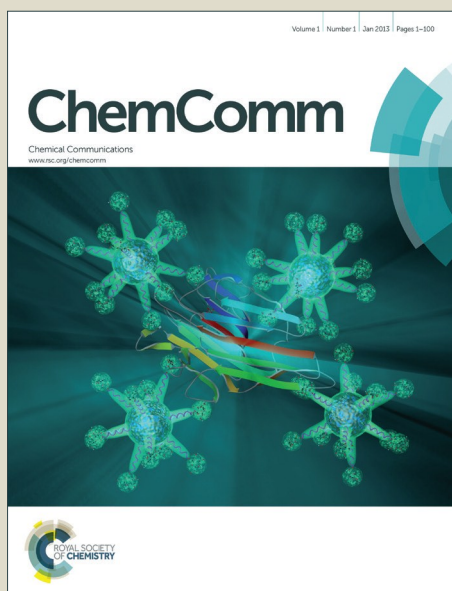


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Preparation of carbon dots by non-focusing pulsed laser irradiation in toluene†

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A simple approach to preparing carbon dots (CDs) by non-focusing pulsed laser irradiation in toluene was presented. The as-prepared CDs were graphite dots which were formed by ablating the intermediate graphene. The size of the as-prepared CDs could be easily controlled by the input of laser fluence. The mechanism of the photoluminescence was also discussed.

Carbon dots (CDs) have been attracting remarkable research interest due to their unique features, such as chemical inertness, a lack of optical blinking, low photo bleaching, low cytotoxicity, and excellent biocompatibility etc¹. And the optical properties are intriguing and vary greatly depending on the fabrication conditions. Several approaches have been developed to prepare CDs, such as chemical ablation, ultrasound or microwave-assisted synthesis, hydrothermal synthesis, and electrochemical etching etc². Among these methods, organic-synthesized CDs are the perfect model to understand the PL mechanism of fluorescent carbon materials, while the complicated synthesis method reduces the possibility for this issue³. Since Sun and co-workers⁴ produced carbon dots by focused laser ablation of carbon targets in water vapour and obtained photoluminescence (PL) by post-passivation, laser ablation was always found to be a fast, effective and not complicated way in CDs preparation⁵. But it remains unclear that the CDs were formed directly from organic carbon source or through intermediate products.

Furthermore the PL properties were the most concerned issue for CDs in view of investigation of the PL mechanism and novel applications. The CDs mainly contained three kinds⁶: graphene quantum dots (GQDs), carbon nanodots (CNDs) and polymer dots (PDs). Despite the diversity of the structures, the CDs possess some similar optical properties on the absorption and fluorescence, such as excitation-dependent emission, size-dependent peak shifts and an emission around 470 nm almost irrespective of excitation

wavelength⁷. The origin of the PL of CDs has been assigned to several reasons in the literature⁸: optical selection of differently sized nanoparticles (quantum effect) defects and surface states, surface groups, surface passivation, fluorophores with different degrees of π conjugation, and recombination of electron-hole pairs localized within small sp² carbon clusters embedded within a sp³ matrix. Although there have been many efforts focused on the physicochemical properties of CNPs, the origin of the observed optoelectronic behaviour is even today a topic of discussion.

In this paper, the toluene was used as carbon precursors to prepare CDs by employing unfocused laser irradiation approach. The formation process of CDs was investigated by monitoring the fluorescence changes of the solution using a real-time detection system. The optical properties and electron dynamics were also studied in CNDs using steady state and time resolved techniques.

Figure 1 shows the schematic illustration of the experimental setup. In the experiment, 5 ml toluene was put into a reaction cell for irradiation. An Nd: YAG non-focusing pulsed laser (Quanta, repetition rate 10 Hz, pulse width 8 ns, beam diameter 8 mm) with a wavelength of 1064 nm was used to irradiate the liquid through a quartz window. Argon gas was used to protect the reaction and keep a safe air pressure. During irradiation, a magnetic stirrer was used to keep the solution homogeneous. Besides, a real-time detection system was used to monitor the fluorescence of the solution, which realized by using a semiconductor continuous laser (wavelength 450 nm) as the excitation source and an optical spectrum instrument (Andor Tech., Mechelle 5000) to collect the emission spectrum. The photoluminescence (PL) and the fourier transform infrared spectrum (FT-IR) of the as-prepared CDs were characterized by a fluorescence spectrophotometer (FP-6500) and a fourier transform infrared spectrometer (VERTEX 70), respectively. Time-resolved fluorescence (TRF) spectra were measured at room temperature by use of time-correlated single photon counting (TCSPC) technique with resolution of 100 ps (Edinburgh FLS920). A small droplet of the prepared sample was deposited on a piece of silicon and a carbon-coated copper grid for Raman (LabRAM HR800) and high-resolution transmission electron microscopy (FEI, Tecnai G2 20) observations, respectively.

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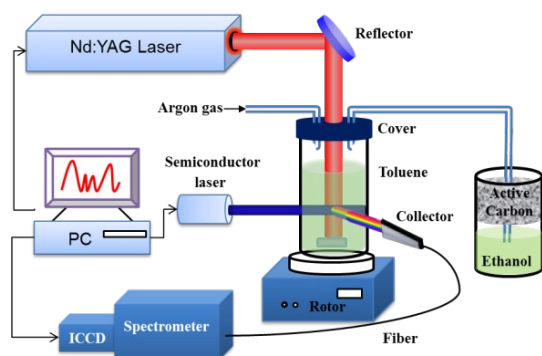


Fig. 1 The Schematic illustration of the experimental setup.

Figure 2 shows the optical spectrum under different irradiation time. It was found that, the intensity of the scattered light around 450 nm increased steadily during the first 3 min, fell down over the next 4 min and touched a low point at 8 min. It is worth to note that, an obvious fluorescence peak over 450 nm~650 nm appeared at 9 min, and then strengthen gradually. This indicated that the different products were generated as the reaction proceeding. It is worth to mention that, after laser irradiating for 15 min, the FT-IR Spectra (Figure S1) of suspension showed the same characteristics as the pure toluene, which confirmed that the solvent after laser irradiation was still toluene.

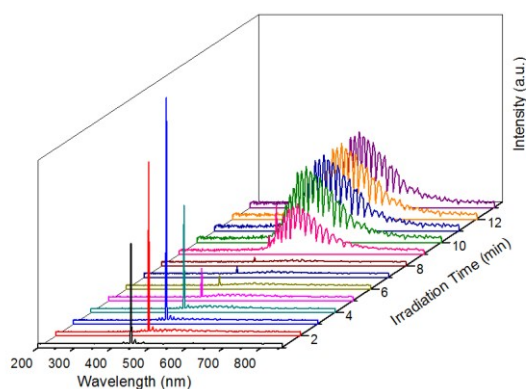


Fig.2 The optical spectra under different irradiation time.

To further study the products that obtained at different stages, two samples were prepared under the irradiation time of 5 min (Marked S-5) and 10 min (Marked S-10). Then, Raman analyses were also taken and shows in the Supplementary Information (Figure S2). The Raman spectrum of S-5 is dominated by two peaks centered at approximately 1364 and 1583 cm^{-1} that can be identified as a defect band (D band) and a graphite band (G band), respectively. However, the strong Photoluminescence of the products masks the Raman spectra for the S-10. Meanwhile, TEM of the S-5 and S-10 were taken to characterize the different products. Figures 3a, b and c show TEM morphologies of S-5 and only a large number of graphene sheets could be found. Fig. 3d shows TEM morphologies of primitive S-10, and curly graphene and nano-agglomerates could be observed. Fig. 3e inset presents the HR-TEM images of the separated carbon nano particles (separation-processes see S3), and well-resolved lattice fringes with an interplanar spacing of 0.25 nm and 0.32 nm were observed, which

is close to the (100) and (020) diffraction facets of graphite⁹. This suggests that the as-prepared CDs are graphite. The schematic illustration of the formation process was display in Fig. 3f. Large piece of graphene were formed at the beginning (For instance, S-5). The graphene increased and superimposed on each other to form large multilayer graphene as the irradiation continuing, followed by the large multilayer graphene was ablated into small CDs by laser irradiation¹⁰. In a word, before generating the CDs, graphene was generated as an intermediate as the reaction proceeding.

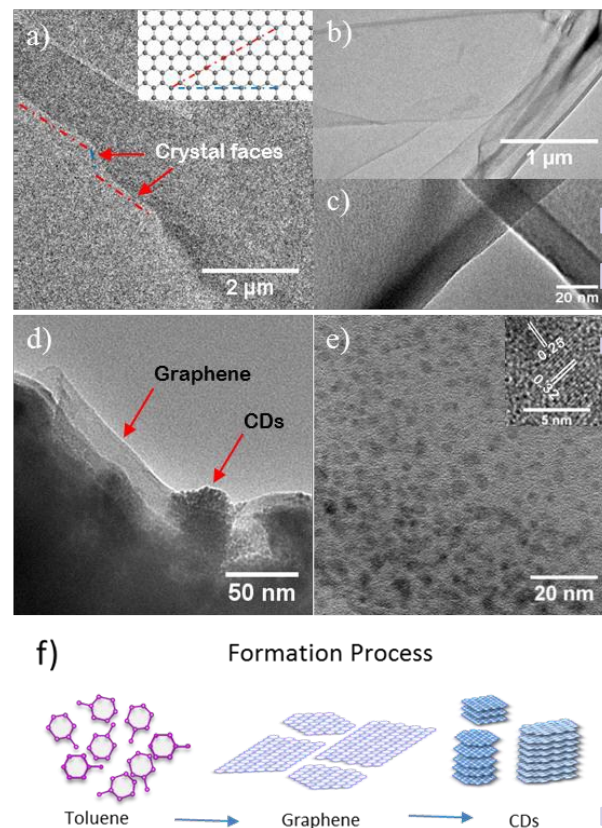


Fig.3 TEM images of the S-5 (a, b, c), S-10 (d, e) and f) the formation process of CDs from toluene. Inset of a) shows that most of the crystal's faces are zigzag and armchair edges as indicated by blue and red lines. Inset of e) is the HR-TEM images of the CDs.

Furthermore, some researchers have found that their optical properties depend on the sizes of CDs; therefore, size control of CDs has become more and more important. Interestingly, the present study clearly demonstrates that the produced CDs have a reasonable size distribution, and further experiments demonstrate this size can be controlled by input laser fluence (Supporting Information, Figure S3). As seen in Figure 4, when the laser fluence is below 350 mJ/pulse the CDs prepared always have controllable size: 2.0-3.9 nm, 3.0-10.0nm, 10.0-17.2nm and 13.0-20. nm corresponding to 100, 200, 300 and 350 mJ/pulse, respectively. If the laser fluence is further increased up to 400 mJ/pulse, two different size distributions (5.7 nm and 77.6 nm) were found (Figure S3e). Moreover, products prepared at 500 mJ/pulse are even diversified, include large unshaped products and hollow spheres (Figure S3f). This indicates that the sizes can be controlled when the laser fluence was below 350 mJ/pulse, but the products are out of control as the laser fluence increased to over 400 mJ/pulse.

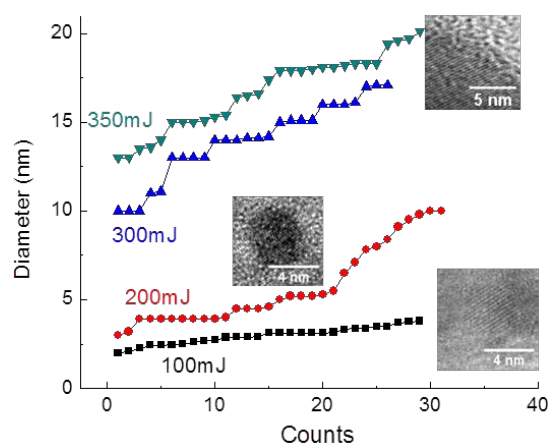


Fig.4 Size distribution under different laser fluence: a) 100 mJ/pulse, b) 200 mJ/pulse, 300 mJ/pulse and 350 mJ/pulse. Insets fluence are the HR-TEM images of different size of typical CDs.

Figure 5 showed the PL and optical observation of the original toluene, S-5, and S-10. Obviously, the colour of the solutions changed from transparent to brown after laser irradiation, and the visible PL was also observed after laser irradiation of the toluene. That is to say, for toluene, the PL was molecular fluorescence and caused by the transition of $\pi^*-\pi$, therefore, the PL emission was at about 330 nm and insensitive to the excitation wavelength. Large piece of graphene were formed at the beginning (For instance, S-5). For this graphene, the conduction band bottom and valence band top intersect at Dirac point and form a zero band gap semiconductors¹¹, hence, the PL emission die out and there was almost no obvious fluorescence for the S-5. It is deemed that the increasing PL intensity (as the irradiation continuing) mainly through promoting CDs synthesis and increasing CDs accumulation. As a result, the S-10 exhibited strong and visible PL (Fig.5b). In order to confirm whether the PL was emitted from the CQDs, the suspension was dried naturally, and then the ethanol was refilled to form another suspension (see S5 in the supplements). The reappearance of PL proved that the PL was emitted from the CQDs and not from the liquid solvent.

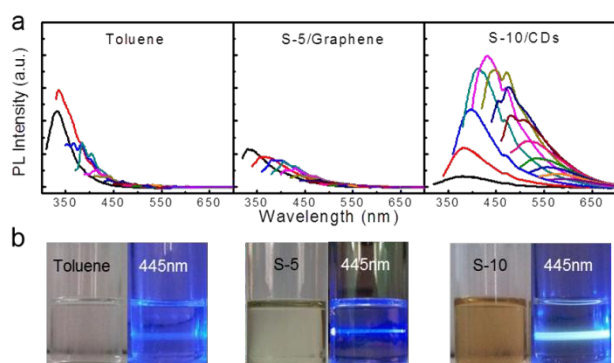


Fig.5 PL spectrum (a) of toluene, S-5 (graphene) and S-10 (CDs), excite at 300-540 nm, 20 nm increments and the visible PL (b) under different periods of the experimental process.

On the other hand, the emission quantum yields excited at 360nm displays a peak value (18%) when the average particle size was about 4.2nm (see S6 in the supplements). These values of emission quantum yield were in the range of the results reported in the literature^{2, 8}. The prepared CDs display low fluorescence

quantum yields, mainly due to very strong absorbance in the UV range and absence of comparable level of absorbance at the visible wavelengths of maxima of excitation spectra (Fig.7a). That is, the CDs exhibit an absence of fluorescence emission excited at the maximum of the UV excitation band, and such behavior is common for carbon dots but is different from that of semiconductor quantum dots¹².

As the laser fluence increasing from 100 mJ/pulse to 350 mJ/pulse, the average particle size increases from 2.9 nm to 16.6 nm (see S4 in the supplements). The absorption spectrum exhibits a peak around 204 nm, a shoulder around 300 nm with a tail extends to 600 nm. As the particle size increasing, the peak around 204 nm is steady, while the shoulder around 300 nm broadened to visible range. The PL main emission shifts to long wavelength (see S7 in the supplements). In a word, the optical properties of the CDs were size-dependent, and it was realized by just changing the irradiated laser fluence. Size-dependent PL is a common phenomenon and could be ascribed to the quantum confinement effect (QCE). Peng et al¹³ prepared three kinds of CDs with different sizes of 1-4 nm, 5-8 nm, 7-11 nm via varying the reaction temperatures, which emitted different PL changing from blue and green to yellow. Interestingly, Kim et al¹⁴ presented size-dependent shape/edge-state variations of CDs and visible PL showing anomalous size dependences, and found that all PL spectra show similar size-dependent peak shifts, almost irrespective of excitation wavelength except 470 nm. Wang's and Yang's¹⁵ groups also report that the PL around 470 nm is different with others. Thus, the state at around 470 nm becomes more and more interesting.

Figure 7c shows the normalized PL spectra of the samples prepared by 200 mJ/pulse. The peak position of the PL spectrum gradually shifts with changes in the excitation wavelength, while a shoulder around 475 nm (P475) is much insensitive to the changing of excitation wavelength. Figure 7(d) summarizes excitation wavelength-dependent PL peak shifts for various-size CDs. All PL spectra show similar size-dependent peak shifts, but exciting between 400 and 450 nm, the PL maximum hardly shifts at all, residing around 475 nm (Fig.7d). Figure 7(e) summarizes excitation-wavelength-dependent PL emission intensity at 475 nm for various-size CDs. As the particle size increasing, the PL maximum excitation wavelength shifts to long wavelength and the emission intensity increases as well. That is, the peak position of P475 insensitive with the particle-size and the excitation-wavelength, but the intensity of the P475 depends on the particle-size and the excitation wavelength. In order to further explore the mechanism of PL, the fluorescence lifetime of P405 and P475 were measured and shown in Fig.6f. For reducing the interference between each other, two excitation wavelengths are adopted at 366 nm and 430 nm, respectively. The photoluminescence lifetime probe at 405 nm is 1.9 ns, whilst the lifetime at around 475 nm is 10.9 ns. Above analyses suggest that a different photochemical mechanism is operating at 475 nm. The singlet-triplet splitting was determined to be ~175 meV, and intersystem crossing was so efficient that it competed with internal conversion among the states with the same multiplicity. As a result, the CDs emit both fluorescence and phosphorescence at room temperature, with their relative intensity depending on the excitation energy¹⁶. The P475 have a significantly longer lifetime and could be ascribed to triplet states. Furthermore,

the size-dependent, discrete excitonic levels could significantly slow down the relaxation of high excited states in CDs due to a phonon bottleneck. In addition, strong carrier-carrier interactions could lead to generation of more than one exciton with one photon absorbed, a process particularly useful for improving the efficiency of photon-generated carrier¹⁷.

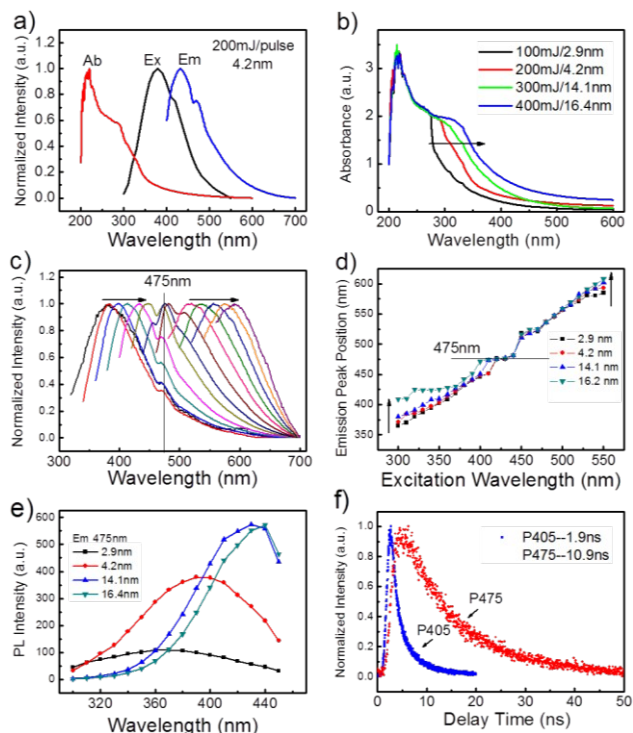


Fig.6 Photoluminescence of the CDs: a) Absorption (red), excitation (black) and emission (blue) spectra of CDs obtained by 200 mJ/pulse; b) The absorption spectrum of CDs prepared under different laser fluence; c) Normalized PL spectrum of CDs obtained by 200 mJ/pulse, excite at 300–540 nm, in 20 nm increments; d) Excitation-wavelength-dependent PL peak shifts for various-size CDs; e) Excitation-wavelength-dependent PL emission intensity at 475 nm for various-size CDs; f) The Photoluminescence lifetime of P405 and P475 of CDs obtained by 200 mJ/pulse.

In summary, a simple approach to preparing (CDs) by non-focusing pulsed laser irradiation in toluene was presented. A real-time detection system was designed to monitoring the fluorescence changes of the solution during the irradiation, and found that the graphene was generated as an intermediate before the CDs were finally produced. This method provides a potential way for fabricating new luminescent materials and an easy way for controlling the fluorescent properties. The as-prepared CDs were graphite dots and exhibited size-dependent PL, which can be controlled by changing the input of laser fluence. The CDs have a significantly longer lifetime of PL and could be ascribed to triplet states.

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