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Effect of laser pulse duration on ultrafast laser synthesis of carbon dots from toluene

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Abstract. Pulsed laser irradiation produces luminescent carbon dots from toluene molecules in liquid medium. We examined influence of laser pulse duration on the rate of synthesis, optical properties and chemical composition of resulting carbon dots. Increase of synthesis rate with longer pulse duration demonstrates that synthesis is mediated by plasma formed through laser breakdown in medium.

Keywords: luminescent carbon dots, femtosecond laser pulses, laser-induced breakdown, nanomaterials

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Материалы конференции

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Влияние длительности лазерного импульса на сверхбыстрый лазерный синтез углеродных точек из толуола

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Аннотация. В данной работе приведены оптические и физико-химические характеристики углеродных точек из толуола, полученных в ходе фемтосекундного лазерного синтеза. Мы исследовали влияние длительности лазерного импульса на скорость синтеза, оптические свойства и химический состав получаемых углеродных точек. Увеличение скорости синтеза с увеличением длительности импульса демонстрирует, что синтез опосредуется плазмой, образующейся в результате лазерного пробоя в среде.

Ключевые слова: люминесцентные углеродные точки, фемтосекундные лазерные импульсы, лазерный пробой, наноматериалы

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Introduction

Carbon nanodots (CNDs) are a promising class of nanomaterials with applications in bioimaging, photocatalysis, light emitting devices and fluorescent sensors. Among various strategies for carbon dots preparation bottom-up pulsed laser synthesis from organic molecules remains little explored [1]. Various authors used laser pulses with duration ranging from tens of femtoseconds to nanoseconds for synthesis of carbon dots from simple aromatic compounds such as benzene or toluene [2–5]. Pulse duration strongly influences both nonlinear absorption and mechanisms of laser synthesis: femtosecond pulses can effectively promote molecules to highly excited states via multiphoton absorption, while longer pulses favour avalanche ionization [6]. Different absorption mechanisms can lead to different reaction pathways and thus affect reaction rate, chemical composition and optical properties of products. However, detailed understanding of these effects in laser synthesis is still lacking. In order to clarify the synthesis mechanism and the role of different nonlinear absorption processes we examined how the pulse duration varied from sub-picosecond to tens picoseconds range affects the rate of synthesis of luminescent carbon dots from toluene. Also, optical and chemical characterization techniques were used to examine the effect of pulse duration on absorption and luminescence characteristics and chemical composition of carbon dots.

Materials and Methods

Synthesis and separation of products. 500 μL of pure toluene in a closed glass flask was irradiated with trains of femtosecond laser pulses focused by a cylindrical lens ($f = 9.7$ mm, 0.3NA) for 10 minutes. Central wavelength of laser pulses was 1033 nm, repetition rate – 1 kHz, pulse energy – 2 mJ, pulse duration in four experiments was 0.25, 1, 3 and 10 ps. After irradiation unreacted toluene was removed by drying; dried samples were then redissolved in ethanol, resulting in yellow and luminescent solutions.

Samples characterization.

Atomic Force Microscopy (AFM) and High-Resolution Transmission Electron Microscopy (HRTEM). Synthesized and dialyzed laser irradiation products in the volume of 1 mL were dissolved in 50 mL of absolute ethanol of HPLC-grade. A drop of the solution was dried on borosilicate glass, which was pretreated with ultraviolet light from a quartz mercury lamp for 10 minutes to clean the surface. Next, the sample was scanned using the AFM unit (SMENA-B, NT-MDT) in an intermittent contact mode.

The HRTEM method was used to image of samples on a JEM 2100F high-resolution transmission electron microscope (JEOL Co., Ltd., Japan) equipped with a spherical and chromatic aberration corrector, an energy-dispersive X-ray spectral analyzer, and an electron energy loss spectrometer (Gatan), measured at an accelerating voltage of 200 kV. Before the measurement, the samples were placed on a copper grid.

Fourier Transform Infrared (FTIR) Spectroscopy. For the spectral measurements, a drop of the dialyzed solution was dried on an aluminum mirror. Infrared absorption spectra were collected using Bruker Lumos II FTIR microscope-spectrometer in a reflection mode with an average of 500 scans.

Raman Spectroscopy. Raman spectra were recorded using a SENTERRA Raman microscope spectrometer (Bruker) with excitation at 785 nm. A drop of sample solution was dried on a silica glass surface and its Raman spectra were recorded with averaging over 200 scans.

Optical Spectroscopy. Absorption spectra of sample solutions in ethanol were measured in a 3.5 mL quartz cuvette using a UV-Vis spectrometer (UV-3600, Shimadzu) and photoluminescence emission (PL) in the same cuvette using a spectrofluorometer (RF-5031PC, Shimadzu). The quantum yield of visible luminescence (excitation at 356 nm) was estimated with the slope

method using anthracene in ethanol (visible fluorescence, $\Phi = 27\%$) or toluene in cyclohexane (ultraviolet fluorescence, excitation at 260 nm, $\Phi = 17\%$) nm as standards. The quantum yield was calculated by the formula $\Phi_x = \Phi_s G_x n_x^2 / G_s n_s^2$, where Φ is a quantum yield, G is a slope of the dependence of the integral luminescence intensity on the value of absorption in solution, n is the refractive index, and subscripts x and s refer to the sample and reference, respectively.

Results and Discussion

Irradiation of toluene with different pulse laser durations (0.25, 1, 3 and 10 ps) led to the formation of colored nanoparticles. The color intensity of the resulting product solution rose with an increasing duration of the laser pulse: from pale yellow to dark brown. The observed darkening of the reaction mixture was accompanied by the formation of a large amount of precipitate. As a result of purification and isolation of the synthesis products colloidal solutions of the high-molecular fraction of the products were obtained, as well as an insoluble precipitate in the form of a dark powder (Fig. 1, *b*).

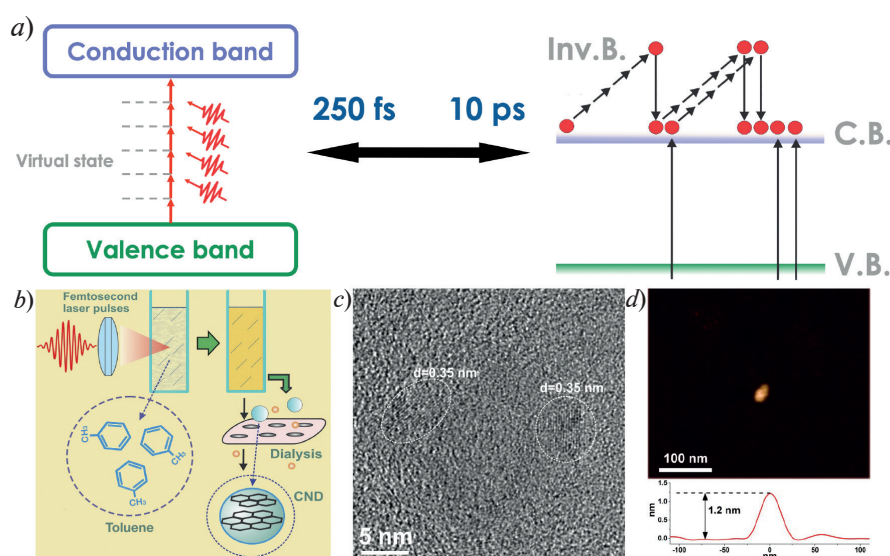


Fig. 1. Schematic illustration of multiphoton absorption and avalanche ionization processes (*a*). Principal scheme of the femtosecond laser synthesis of CNDs from toluene and purification of CNDs (*b*). HRTEM image of CNDs from toluene illustrating types of observed crystalline structure of carbon nanodots (*c*). AFM image of toluene CND lying on a glass substrate and representative height of CNDs, measured from the AFM scan (*d*)

By changing the femtosecond laser parameter, such as the laser pulse duration from 250 femtoseconds to 10 picoseconds, we synthesized carbon nanomaterials with varying ratio nonlinear processes: multiphoton absorption and avalanche ionization (Fig. 1, *a*). Toluene can absorb 1033-nm laser wavelength by four photon absorption with intensity scaling as a fourth power of intensity. On the other hand, the rate of impact ionization is approximately proportional to the laser intensity [6]. By tuning the femtosecond laser to a pulse duration of 250 femtoseconds and a central wavelength of laser of 1033 nm, we have a high-intensity light source in which toluene absorb several photons of light simultaneously. On the other hand, during the transition from high-intensity light fields to less intense (10 picoseconds), we observe avalanche ionization. Avalanche ionization occurs when a single electron in toluene is excited by a photon of light and gains enough energy to ionize other electrons in the dot through collisions. This process leads to the rapid multiplication of free electrons in the dot, resulting in a phenomenon known as an avalanche ionization. Different photoexcitation processes can result in different reaction pathways and thus influence physiochemical properties of resulting CNDs. Ultimately, the samples obtained at different laser pulse durations were sent to study the chemical composition and morphology, as well as optical properties.

Characterization of the toluene product using atomic force microscopy (AFM) showed that it consists of nanoscale particles whose size was within a few nanometers (Fig. 1, *d*).

The HRTEM morphology analysis (Fig. 1, *c*) of carbon nanomaterials revealed that the composition of the soluble fraction contained nanoparticles with a characteristic parallel layers crystalline structure with a lattice period of 0.35 nm. These lattice parameters are close to the interlayer spacing (0.335 nm) of the crystalline lattice of graphite. Thus, the nanoparticles formed as a result of laser synthesis had a graphite-like crystalline structure.

In order to get more information about the nature of obtained carbon nanomaterials, we used the Raman spectroscopy (Fig. 2, *b*). Raman spectra exhibited strongest peaks at ca. 1000 (breathing vibrations of isolated aromatic rings), 1600 cm⁻¹ (C = C stretching in isolated and fused rings) and 2100–2200 cm⁻¹ (C ≡ C stretching vibrations). The ratio between peaks demonstrated relative decrease of isolated rings and increase of fused rings and alkynes content with longer pulse durations. Thus, the new material contained a significant amount of sp² C atoms and graphite-like domains comprising hexagonal aromatic rings. It is curious to note that with an increase in the duration of the laser pulse, a product had fewer aromatic rings and more unsaturated sp-hybridization carbon domains with a triple bond in its composition. We have confirmed the partial graphitization of the obtained carbon nanomaterials and claim that it can be described as carbon nanodots.

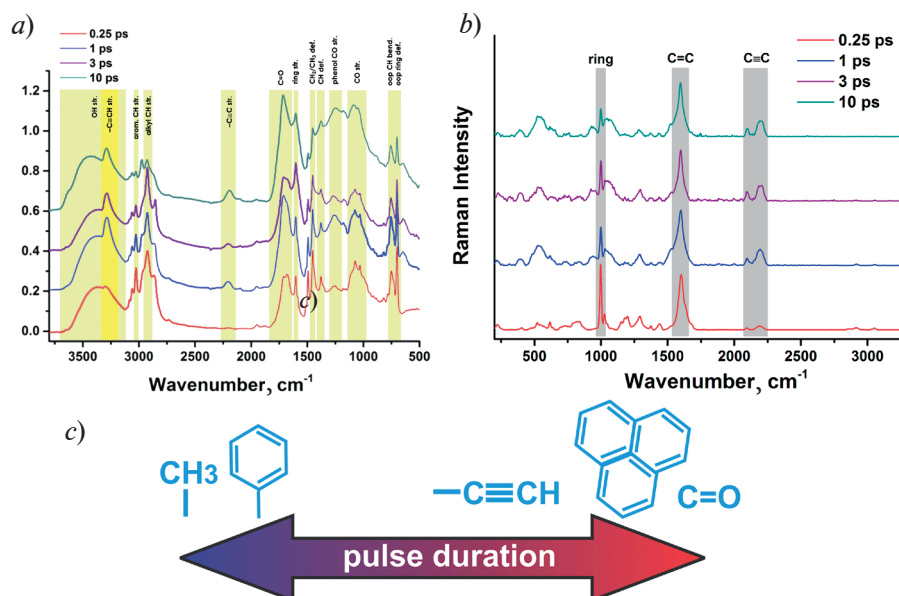


Fig. 2. FTIR reflectance spectra of toluene CNDs obtained at 0.25, 1, 3 and 10 ps (*a*). Raman spectra of toluene CNDs obtained at 0.25, 1, 3 and 10 ps (*b*). Schematic illustration of the change in the chemical composition of CNDs from the laser pulse duration (*c*)

FTIR spectroscopy revealed presence of similar functional groups in all carbon dots samples: aromatic CH stretching peaks between 3000 and 3100 cm⁻¹, alkyl CH stretching peaks near 2850 and 2950 cm⁻¹, a series of sharp aromatic ring stretching peaks between 1400 and 1495 cm⁻¹, out-of-plane CH bending peaks at 710–750 cm⁻¹, an aromatic ring deformation peak near 700 cm⁻¹ (Fig. 2, *a*). Broad OH (3600–3000 cm⁻¹) and C = O (ca. 1700 cm⁻¹) stretching peaks confirms presence of oxygen in CNDs as a result of oxidation. Also, the presence of a triple bond was revealed in all samples of carbon dots (monosubstituted alkynes – C ≡ CH about 3280–3340 cm⁻¹ and C ≡ C about 2160–2255 cm⁻¹). We observed that the duration of the laser pulse affected the chemical composition of the carbon dots. The strength of hydroxyl and carbonyl bands (3100–3600 cm⁻¹ and 1650–1800 cm⁻¹, respectively) increased, whereas the strength of aromatic ring and alkyls vibrations decreased at longer pulse durations. In conclusion, vibrational spectroscopy demonstrates that the pulse duration strongly influences composition of functional groups of CNDs.

Next, we examined the optical properties of toluene carbon nanodots. Carbon dots samples obtained at different pulse duration had similar optical properties: strong UV absorption, strong structured luminescence in the UV range with emission maximum at 318 nm and much weaker

visible luminescence in the blue spectral region (Fig. 3, *a*). Toluene absorbs light in the far UV range and does not emit visible luminescence. At the same time CNs obtained from toluene exhibited strong absorption in the near-UV and visible range and emitted bright blue luminescence when excited at ca. 350 nm (Fig. 3, *b, d*). The strength of absorption and intensity of luminescence per sample volume depended on the laser pulse duration and increased several times when the duration was tuned from 250 fs to 10 ps, other condition being equal. This effect was in accord with deeper color of toluene samples irradiated with longer laser pulses. For the 10 ps laser pulses of the same energy the peak intensity is 40 times lower than for the 250 fs pulses, and correspondingly the rate of multiphoton absorption is orders of magnitude smaller. Still the rate of carbon dots production for 10 ps pulses was several times larger. This fact indicates that the avalanche ionization and chemical reactions, mediated by free electrons produced by ionization, make large contribution to process of carbon dots synthesis.

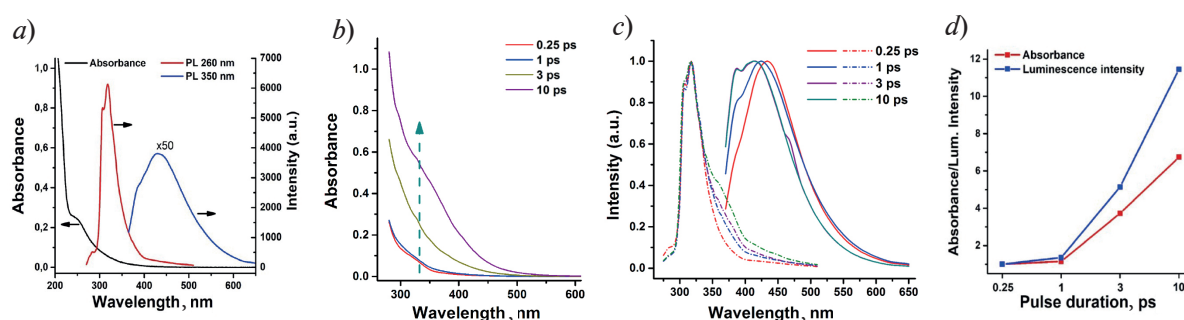


Fig. 3. General optical properties (UV-Vis absorption spectrum and PL spectra) of toluene CNs obtained at different laser pulse duration (*a*). UV-Vis absorption spectra of toluene CNs at different laser pulse durations (*b*). UV-PL and Vis-PL spectra of toluene CNs at different laser pulse durations (*c*). Absorbance and PL integral intensity of toluene CNs obtained at 0.25 ps, 1 ps, 3 ps and 10 ps (*d*)

Analysis of absorption and luminescence spectra demonstrated that carbon dots obtained at different pulse duration had generally similar optical properties. They all had broad absorption spectra with an absorption peak in the far UV-range, attributed to $\pi-\pi^*$ absorption in the aromatic structures, and a weaker absorption tail in the near-UV and visible region attributed to $n-\pi^*$ absorption. With increase of the pulse duration the UV absorption peak became more prominent and shifted to the blue side from ca. 260 to ca. 240 nm. This position of the absorption peak is indicative of graphene structures strongly disordered by oxidation such as graphene oxide. All CNs emitted strong UV luminescence with a structured emission spectrum, peak emission at 318 and peak excitation at 260 nm. We believe that this UV emission originated from bitoluene groups within CNs. While the emission and excitation peaks were unchanged the measured quantum yield of the UV luminescence increased from 25.6% to 35.1% when the laser pulses were stretched from 0.25 to 10 ps (Table). In addition to UV luminescence all CNs emitted much weaker blue luminescence, which is likely attributed to oxidation of CNs in presence of atmospheric air and formation of multiple oxygen-containing functional groups [5].

Table

Main parameters of fluorescence of t-CNs

	0.25 ps	1 ps	3 ps	10 ps
QY (%) (exc. at 260 nm)	25.6	23.9	32.3	35.1
QY (%) (exc. at 356 nm)	2.88	2.6	5.07	5.24
Maximum PL (nm) (exc. at 356 nm)	425	439	416	415

Pulse duration influenced both the quantum yield of this blue emission, which increased almost two-fold with transition from 0.25 to 10 ps (Table), and emission spectra. As illustrated by the Fig. 3, *c* with increase of the pulse duration the emission maximum shifted from ca. 439 to ca. 415 nm. It seems likely that changes in chemical groups of CNs, registered by



FTIR spectroscopy, affect characteristics of visible luminescence. As a result, a different set of chromospheres contributes to visible emission of CNDs produced at different laser pulse duration.

Conclusions

Irradiation of liquid toluene with laser pulses of duration ranging from hundreds femtoseconds to tens picoseconds produces carbon dots with mostly similar optical properties. Longer laser pulses of the same energy produced carbon dots with larger rate. This fact suggests that synthesis is mediated by electronic plasma formed by avalanche ionization in medium. Optical properties and chemical composition of carbon dots can be manipulated by pulse duration. Nanoparticles synthesized by longer pulses exhibit higher fluorescence quantum yield and thus are more attractive for practical applications.

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