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Stepanova, M.; Dubavik, A.; Skurlov, I.; Zakharov, V.; Rogach, A.

Published in:

Journal of Physics: Conference Series

Published: 01/01/2021

Document Version:

Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

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Publication record in CityU Scholars:

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Published version (DOI):

[10.1088/1742-6596/1866/1/012005](https://doi.org/10.1088/1742-6596/1866/1/012005)

Publication details:

Stepanova, M., Dubavik, A., Skurlov, I., Zakharov, V., & Rogach, A. (2021). Surface modification of carbon dots by UV laser radiation. *Journal of Physics: Conference Series*, 1866, Article 012005.
<https://doi.org/10.1088/1742-6596/1866/1/012005>

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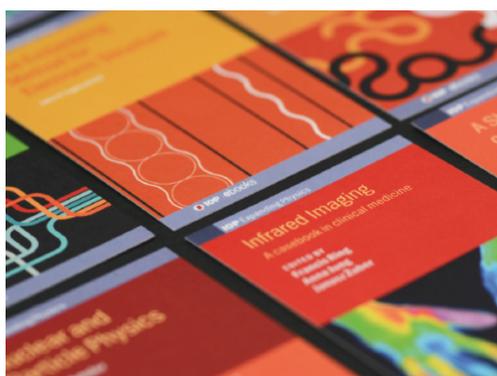
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To cite this article: M Stepanova *et al* 2021 *J. Phys.: Conf. Ser.* **1866** 012005

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Surface modification of carbon dots by UV laser radiation

M Stepanova¹, A Dubavik¹, I Skurlov¹, V Zakharov¹ and A Rogach²

¹ ITMO University, Russia

² City University of Hong Kong, Hong Kong

mary.s.stepanova@gmail.com

Abstract. Carbon dots have been modified using UV irradiation (405 nm laser light). UV irradiation of carbon dots has led to various changes in optical properties, which in turn means photomodification of the carbon dots surface. With an increase in light transmission, we have obtained the increasing intensity of photoluminescence and a blue shift by the laser irradiation of the carbon dots. The proposed method can help to adapt and improve the optical properties of carbon dots and can be used in applications, for example, in the optical encryption field.

1. Introduction

Carbon dots (CDs) represent a promising class of carbon-based luminescent nanomaterials due to their simple and cheap synthesis, high biocompatibility, and photostability. With attractive optical properties, CDs have a great potential to be used as fluorescent sensors for the detection of various analytes [1], solar cells [2], light-emitting devices (LEDs) [3], as well as for stem cells' imaging (bioimaging), and photodynamic therapy of cancer [4]. A lot of studies have been performed to identify the mechanism of photoluminescence (PL) of CDs and the dependence of their emission on the CDs' structural characteristics. The emission of CDs can be assumed to be caused by polycyclic aromatic hydrocarbons (PAHs) [5,6-8]; organic dyes are embedded in an amorphous matrix [9]; doping of CDs with heteroatoms containing single and double bonds [10-12]. However, the nature of electronic transitions in CDs is not completely understood yet. Some certain parameters of synthesis, namely, precursors, temperature and pressure affect the carbonation degree and the type of luminescent centers inside CDs. Consequently, the energy structure of CDs also depends on the synthesis pathways. Moreover, some synthesis routes allow obtaining CD, which PL depends on excitation. The ability to change the radiation wavelength is attributed to the selective excitation of CDs subsets in a CDs ensemble [13]. It was shown in [14] that the radiation excited by wavelengths of 488, 561, 640 nm originates from various particles. On the other hand, it is assumed in [15] that, within a single CD, different luminescent centers are responsible for the excitation-dependent radiation. In [15] the authors used single-dot PL spectroscopy and showed that a single CD exhibits the excitation-dependent PL spectra. Besides, from the PL images of the same region of the sample excited by three lasers with different wavelengths, it can be seen that CDs in total contain the least number of CDs with long-wavelength emitting centers.

The dependence of the optical properties on functional groups on the CDs surface is also of great interest. The potential effect of molecular fluorophores on the optical properties of CDs has been also reported [9]. Thus, the CDs' optical properties can be changed or improved by the surface modification



of the dots. There are various ways to modify the CDs surface, for example, using a solvothermal process in different solvents [16], since the formation of functional groups depends on the chemical properties of the solvent, the heating time, and the purification method. The creation of composites by grouping the CDs and other functional materials into one microarray can change the CDs' surface [17]. Photoirradiation can be one of the ways to change the surface of dots. While the emitting of molecular fluorophores and surface states of CD has a weak photostability, the core emitting is resistant to photobleaching [18]. Based on the difference in photostability, it has been demonstrated how the CDs surface can be deoxidized by prolonged ultraviolet irradiation.

2. Materials and Methods

2.1. Materials

Citric acid and ethylenediamine were purchased from Sigma-Aldrich. All reagents were used without any changes. Ultrapure water (Milli-Q) was used throughout the experiments.

2.2. Synthesis of CDs

CDs were synthesized following a standard hydrothermal procedure. Citric Acid (1.05 g, 5.5 mmol) and an amine precursor (335 μ L of ethylenediamine) were dissolved in 10 mL of distilled water to form a transparent solution. Then, the solution was transferred into a poly(p-phenol)-lined stainless steel autoclave for the solvothermal reaction. The stainless autoclave was held at a temperature of 200°C for 5 h. After the autoclave was cooled to room temperature, the reaction products were filtered and centrifuged at 500 rpm for 10 min to separate them from the agglomerated larger particles. Then CDs were redissolved in water for further measurements.

2.3. Characterization

Absorption and photoluminescence spectra were recorded using a spectrophotometer UV-3600 (Shimadzu) and spectrofluorometer Cary Eclipse. Images and local spectra of PL were recorded using an LSM 710 confocal laser scanning fluorescence microscope based on the upright stand the Axio Imager Z1 (Carl Zeiss, Germany) and a 20x/0.75 lens. A 405 nm diode laser has been used as an excitation source. Spectrally resolved images were recorded with a 32-channel photodetector.

3. Results and discussion

The film of CDs, which was obtained by the evaporation method from an aqueous solution with a high concentration of CDs, was used as a sample of the dry layer. As shown in figure 1, the prepared CDs in the solution and the dry layer have various spectral properties. The photoluminescence peak position of the solution is 470 nm, while the photoluminescence peak position of the film is 600 nm. The photoluminescence band maximum in the dry layer has a long-wavelength shift of 130 nm relative to the solution. A similar effect is observed for the absorption peak in the dry layer, which has a slight long-wavelength shift of 5 nm relative to the solution. The emission band maximum shifted to the longer wavelengths as the sample was drying up due to reabsorption and Förster energy transfer between dots in the dry layer.

As an irradiation result of a CDs film part with a 405 nm laser, an increase in the photoluminescence intensity and light transmission was simultaneously observed with a shift to the short-wavelength of photoluminescence. A shift of the photoluminescence maximum is 35 nm with an increase in the photoluminescence intensity by more than two times. The exact amount of offset and increase in PL intensity depends on the laser exposure time. However, the optical properties that are changed during this process have a certain value, after which no changes occur. The corresponding fluorescence images were obtained using a confocal laser scanning microscope (inset in figure 2). Absorption and photoluminescence spectra of the background (black line) and UV-irradiated regions (red and blue lines) of the CDs film are demonstrated in figure 2.

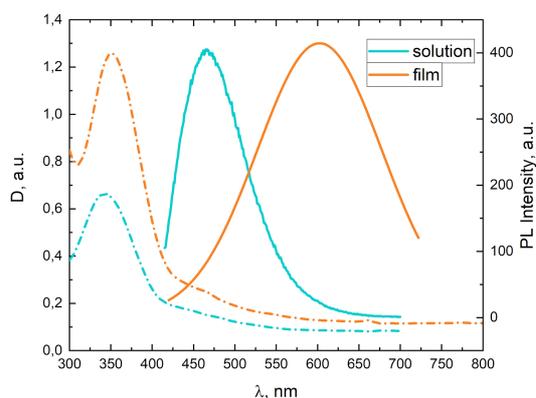


Figure 1. Normalized absorption and PL spectra of a solution (blue line) and a film (orange line) of CDs.

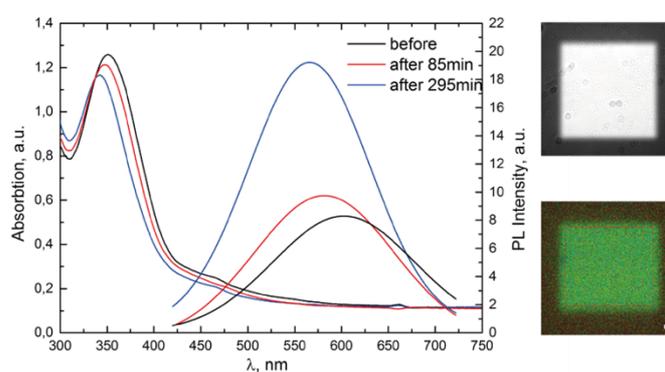


Figure 2. The absorption and PL spectra of the background (black line) and UV-irradiated region after 85 min (red line) and 295 min (blue line) of the CDs film, the image of the corresponding areas is shown on the left.

The laser radiation exposure leads to the CDs' surface modification, which is confirmed by the spectral changes in the long-wavelength photoluminescence. In addition, the absorption peak shift by 10 nm and a decrease in optical density at a wavelength of 350 nm is detected. Under the intense laser action, photodegradation of organic compounds occurs; however, in the case of nanoparticles, photodegradation begins from the surface. Since changes are observed in the long-wavelength region of the spectrum, the surface luminophores responsible for long-wave photoluminescence are destroyed within the process of laser exposure. The carbon dot contains luminophores emitting at various wavelengths, and the condition for the energy transfer between the luminophores is fulfilled. Consequently, with the degradation of “red” surface luminophores, the conditions for energy transfer change, which in turn leads to an increase in shorter-wavelength photoluminescence.

4. Conclusion

Finally, we have demonstrated one of the methods for modifying the CDs surface by destroying surface-emitting centers under the action of laser irradiation using the example of the most widespread carbon dots. A model has been proposed to describe the observed effect based on the change in the energy transfer between the luminescent centers inside a carbon dot. The energy transfer redistribution occurs due to the photodegradation of surface luminophores. The proposed method can help to adapt and improve the optical properties of carbon dots. Moreover, this method can be used to implement carbon dots into such applications as light-emitting devices, biomarkers and others. The discovered effect can be also used in the field of optical encryption.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, goszadanie no. 2019-1080 and financially supported by the Government of the Russian Federation, Grant 08-08.

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