6th CONFERENCE ON NANO- AND MICROMECHANICS
3-5 JULY 2019 - RZESZÓW, POLAND

Functionalization of carbon nanodots in liquids using laser ablation method

Agata Kaczmarek [a) *], Artur Małolepszy [b)], Jacek Hoffman [a)], Justyna Chrzanowska-Giżyńska [a)], Sławomir Błoński[a)], Zygmunt Szymański [a)], Tomasz Mościcki [a)]

[a)] Institute of Fundamental Technological Research PAS, Pawinskiego 5B,Warsaw, 02-106, Poland

[b)] Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warynskiego 1, Warsaw, 00-645, Poland

akaczmar @ippt.pan.pl

Keywords: carbon nanoparticles, C-dots, laser ablation in liquid, photoluminescence

Luminescent carbon dots were synthesized by the laser ablation in several liquids like polyethylene glycol (PEG), triethanolamine (TEA) that contain different functional groups. The ablation either of carbon target submerged in liquid (two-step laser irradiation: first graphite target, next obtained suspension [1]) or in a suspension of expandable graphite flakes in liquid were made. Both methods revealed comparable very effective production of CDots.

Next the analysis of synthesized nanoparticles were performed including particle size measurements (DLS, HRTEM) and their optical properties including absorbance, photoluminescence as well as identification of functional groups attached to the CDots surface (FTIR, XPS). The exemplary size-distribution of carbon particles are presented in Fig. 1b, 1c.

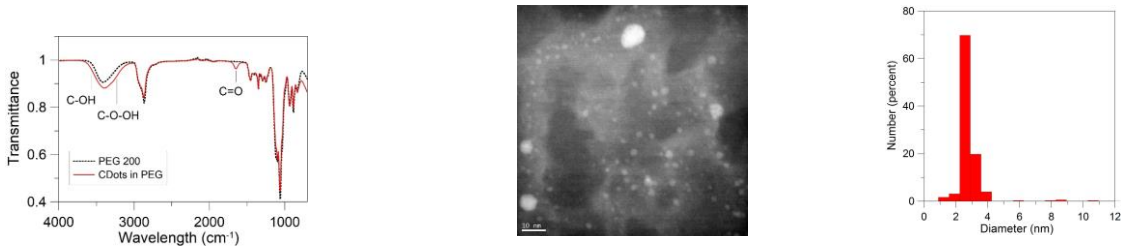

Fig.1. a) FTIR spectra; solid line - suspension of CDots in PEG200, dotted line – PEG200, b) HR-TEM images (HAADF- STEM), c) particle size-distribution derived from the HRTEM images.

Fig. 1a shows the FTIR spectra of CNPs suspended in PEG_{200}. The intrinsic features of CDots spectrum are overshadowed by the absorption of PEG and can be well seen only where the IR absorption of PEG is close to zero like absorption peak C=O observed at 1650 cm^{-1}. Nevertheless the appearance of new functional groups on the CDots surface is clearly manifested by the increased absorption in the region 3000 - 3600 cm^{-1} due to the presence of the C−OH bond and the C−O−OH carboxylic group.

Optical properties were made using the absorption and fluorescence spectroscopy. The absorbance of carbon nanoparticles were measured with a spectrophotometer (Thermo Scientific

Multiscan GO). The absorbance of CNPs is obtained from the suspension by subtracting the absorbance of pure liquid (PEG200 or other). The effect of different reagents is already seen in Fig.2 where the differences in absorbance of CDots synthesized in PEG 200 and TEA are shown. CDots synthesized in PEG show a strong absorption peak located at 220 nm corresponding to the photon energy of 5.43 eV, associated with the transition $\pi-\pi^*$ of aromatic C=C bonds in carbonic core and a shoulder at ~ 260 nm (4.77 eV) corresponding to n - π^* transition of the C=O bond while CDots in TEA show peaks at 228, 280, and 320 and 375 nm from different transitions are observed revealing the attachment od different functional groups containing hydrocarbon or amine chains.

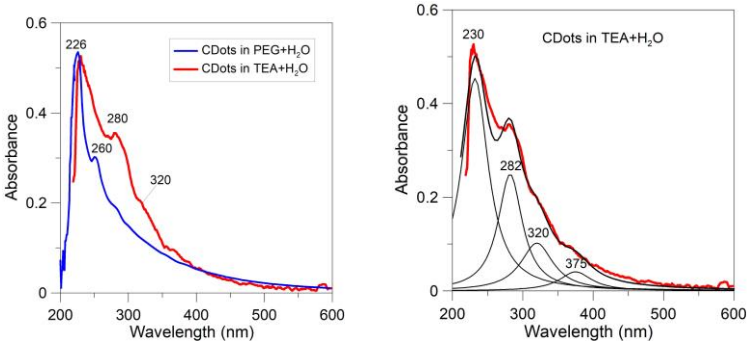

Fig.2 Absorbance CDots in PEG and TEA a), deconvolution of peaks in TEA - right b)

The photoluminescence spectra were recorded with the use of a Fluorescence Spectrometer (FS 5 Edinburgh Instruments). The photoluminescence spectra of synthesized CNPs suspended in PEG_{200} and TEA are presented in Fig. 3. CDots in TEA were diluted in water and excited at 320, 335, 350, 370, 400, 420, 450,500 and 550 nm. Due to dilution the photoluminescence intensity is lower than that of undiluted CDots in PEG. It is clearly seen that the use of amine containing TEA results in the increase of absorption at 230-400 nm wavelength and consequently in the shift of maximum photoluminescence from 320-330 nm observed in the case of PEG to 400-420 nm in the case TEA.

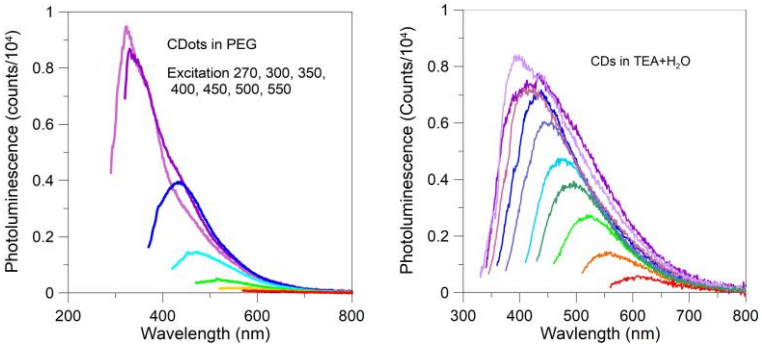

Fig.3. Photoluminescence spectra of carbon nanoparticles (CNPs) suspended in PEG_{200} and TEA. CDots in TEA were diluted in water and excited at 320, 335, 350, 370, 400, 420, 450,500 and 550 nm.

The preliminary results on functionalization of carbon nanodots using laser ablation of carbon in in passivating fluids shows possibility of synthetizing of photoluminescent Cdots. For fluorescent bio-imaging better absorption farther in the red spectral region is necessary [2].

References

[1] A. Małolepszy, S. Błoński, J. Chrzanowska-Giżyńska, M. Wojasiński, T. Płociński, L. Stobiński, Z. Szymański, Fluorescent carbon and graphene oxide nanoparticles synthesized by

the laser ablation in liquid, Appl Phys A Mater Sci Process 124 (2018) 282 doi: 10.1007/s00339-018-1711-5
[2] R. Jelinek, Carbon Quantum Dots. Synthesis, Properties and Applications (Springer, 2017).
Submission highlights:

Since CDots permeate through the leaky tumor vasculature to a higher degree than through the healthy tissue and remain in the area they can be used for signaling or therapy. The key parameter of fluorescent nanoparticles is their quantum efficiency. Since the so-called “biological window“ is between 650-950 nm the effort is concentrate on achieving CDots with high quantum yield in this region which is essential for using them as diagnostic agents. In this paper, the results of synthesis of luminescent carbon dots with diameter 2 to 8 nm, performed by interaction of a nanosecond laser pulse with the suspension of graphite in various viscous liquids like polyethylene glycol (PEG) and triethanolamine (TEA) are presented.