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Innovative electroluminescent nanocomposites for a new approach in polymer based light emitting devices

Project no.: 335/5.10.2011

Stage V (2016)

Scientific report

In this last stage, the research activities were mainly focused in obtaining a complete set of investigations related to the prepared Carbon Dots prepared in the previous stages. Thus, several valuable conclusions were drawn regarding their structural configuration and about the luminescence mechanism involved in the radiative processes. The completion of the research allowed the publication in *Springer-Journal of Material Science* of an extended study regarding the new Carbon Dots prepared by pyrolitic processing of N-Hydroxyphthalimide and a series of new highly luminescent polymer composites.

As mentioned in a previous scientific research report (stage III) these Carbon Dots allows the implementation in various applications due to their impressive emissive properties (PLQY=79,9%) which are between the best results internationally reported so far. Therefore, the additional studies were focused on:

- *Morphology of the prepared Carbon Dots*

HR-TEM microscopy revealed the most comprehensive information regarding the size and tendency of clustering of the prepared C-Dots. **Figure 1(a,b)** presents the recorded micrographs at two different resolutions. Figure **1.a** confirmed the clustering tendency of the prepared C-Dots with an average size of the clusters in 100-300 nm range. The most important aspect which is clearly highlighted by the recorded images, is the existence of smaller (20-30 nm), almost spherical shaped entities within the cluster. While their aspect could suggest individual C-Dots, it is also possible to be attributed to even smaller clusters further organised in larger ones. The second image recorded at higher resolution (Figure **1.b**) revealed the existence of even smaller entities in 2-4 nm range which could highlight the individual C-Dots but, one can not exclude the hypothesis that these very small entities to be also nano-clusters. Therefore, there is the possibility that individual Carbon Dots to be even smaller which could bring to a certain extent some support for the luminescence mechanism based on dimensional influence in a similar behaviour with the semiconductor Quantum Dots.

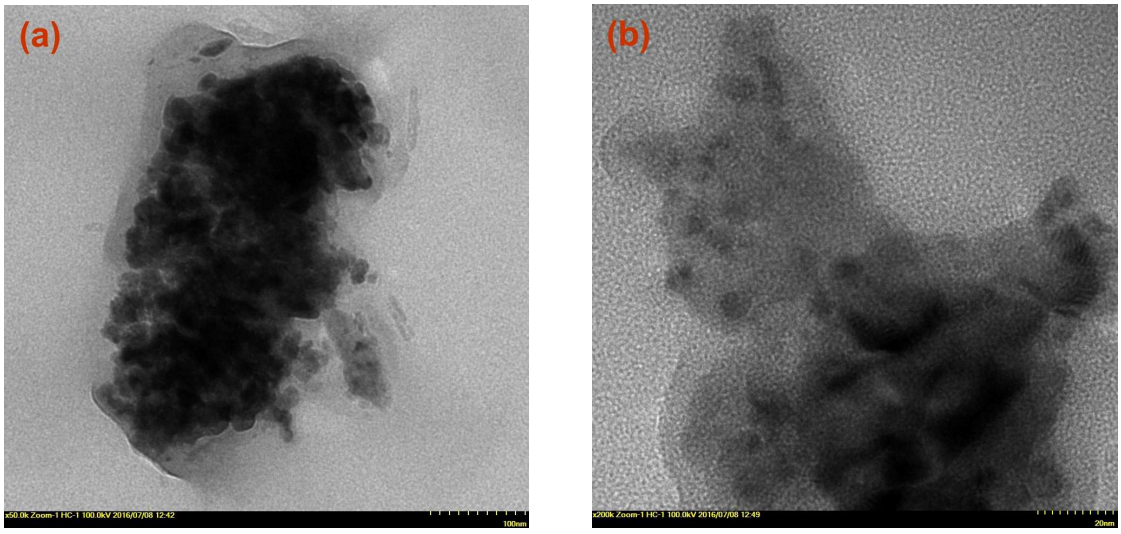

Figure 1. Recorded HR-TEM images of the prepared Carbon Dots

- Influence of the dispersion medium over the PL properties of the prepared Carbon Dots

As previously mentioned, there is a significant dependence of the emission peaks location and radiative processes efficiency by the solvent used as dispersion media. Therefore the study over this influence was extended, several interesting and significant conclusions being obtained. This solvent dependence of the emission peaks and PLQY was also observed in case of C-Dots prepared in our previous work where N-Hydroxysuccinimide was used as precursor [2] and may provide an additional support in favor of the PL mechanism relying mainly on radiative transitions occurring within or between the functional groups located on the C-Dots surface and only indirect related to the size of the carbonaceous core. However, in certain studies the excitation wavelength dependent emission peaks are explained by the simultaneous presence of C-Dots with various dimensional characteristics of the carbonaceous core, each responsible for a particular emission peak. In the view provided by the results presented in the present work, this approach is less capable to explain the notable differences in terms of recorded PLQY between various solvents used to disperse the C-Dots.

For a better understanding of the influence of the dispersion solvent over the emission efficiency of the radiative processes, the newly prepared Carbon were dispersed in a series of commonly used solvents, as detailed in **Table 1**. The highest recorded PLQY value (79,9%) is noted for C-Dots dispersed in chloroform in the non-polar solvents group. In case of polar aprotic and non-polar solvents, the emission efficiency is in a direct relation with the polarity index. The smallest value was recorded in N-Hexane but, this could be a result of the observed poorer dispersion of the C-Dots in this solvent. In all cases, with the exception of N-Hexane dispersed C-Dots, the highest PLQY values were recorded at 380-390 nm excitation wavelengths. Therefore, the recorded results seems to bring strong arguments for the PL mechanism based on functional groups which is able to better explain it on the basis of the

excited states achieved within or between surface located functional groups responsible for various trapping states with different energy levels leading to the excitation dependent emission strongly influenced by the surrounding solvents. Such great difference of the recorded PLQY values is better supported by the interactions occurring between the solvent and the surface located functional groups which in a particular case may favorize the radiative transitions responsible for the PL emission or may provide conditions for non-radiative deactivation paths leading to a less intense PL emission.

Table 1. Absolute PLQY of the C-Dots dispersed in various solvents

NHF C-Dots/ dispersion solvent	**Solvent type***	**Solvent Polarity Index***	**Excitation (nm)**									
			330	**340**	**350**	**360**	**370**	**380**	**390**	**400**	**410**	**420**
			PLQY (%)									
C-Dots/H_2O	Polar protic	9.0	-	-	8.7	8.6	8.2	9.3	**11.1**	10.7	-	-
C-Dots/EtOH		5.2	-	-	28.6	29.5	27.8	**30.6**	28.8	29.5	-	-
C-Dots/DMSO	Polar aprotic	7.2	32.6	46.7	54.7	54.3	47.9	53.8	**59.5**	57.3	48.9	37.6
C-Dots/acetone		5.1	-	-	30.3	36.2	28.4	39.8	**50.6**	-	-	-
C-Dots/THF		4.0	35.3	43.7	38.6	37.1	34.6	42.2	**44.6**	37.5	22.7	12.0
C-Dots/ chloroform	Non-polar	4.1	34.3	43.7	49.6	51.8	56.2	60.2	**79.9**	69.9	47.8	25.0
C-Dots/ethyl ether		2.8	29.3	37.7		43.6	43.7	49.8	**54.5**	39.9	24.8	16.3
C-Dots/benzene		2.7	-	-	5.5	7.3	9.4	12.2	**12.6**	8.6	3.9	-
C-Dots/N-Hexane		0.0	5.43	**10.7**	8.2	5.3	4.4	6.6	5.3	3.5	3.9	3.6

The greatly improved PLQY of the Carbon Dots prepared using N-Hydroxyphthalimide as precursor, compared to our previous study of Carbon Dots derived from N-Hydroxysuccinimide could be explained by the presence of the aromatic ring in the precursor structure, which through thermal processing may favorize a better configuration of the surface located functional groups or a more efficient harvesting of the excitation energy which is subsequently transferred to excited states responsible for the radiative processes. Interestingly, the presence of aromatic ring in the precursor which due to the structural re-arrangements occurring through thermal processing could explain the impressive results in terms of luminescent properties.

The recorded fluorescence lifetime (**Figure 2**) of the prepared Carbon Dots dispersed in chloroform was found in the 4.5-6 ns range which is in accordance with other studies related to fluorescent carbon nanostructures.

As presented in our previous reports, the chromaticity parameters of the prepared Carbon Dots are strongly dependent both on the excitation wavelengths and dispersion solvent. The later studies performed over the Carbon Dots prepared from N-Hydroxyphthalimide additionally confirmed this dependence by the dispersion medium, as could be noticed **from Figure 3(a-d)**. where the chromaticity parameters according to CIE1931 standard are presented.

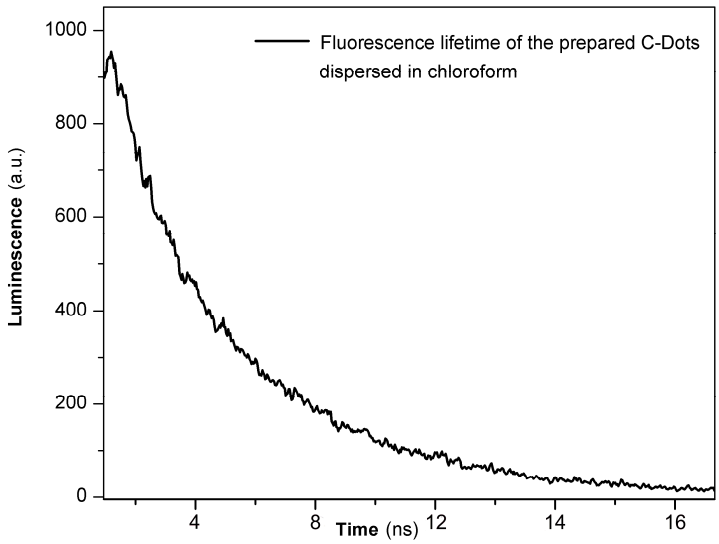

Figure 2. Fluorescence lifetime recorded for the prepared Carbon Dots prepared from N-Hydroxyphthalimide dispersed in chloroform

For the water dispersed Carbon Dots the recorded chromaticity parameters define the overall emission color in the upper interval of the green area of the visible spectrum. For the rest of the dispersion mediums (THF, chloroform, acetone) the emission is located in the blue area of the visible spectrum with the most intense bluish tinted emission recorded for the Carbon Dots dispersed in THF. In all the cases the spectral purity of the emission is not very high due to the specific configuration of the emission peaks.

During the research program related to the main goals of the project, a number of conclusions were drawn which optimize the obtained composites for the targeted applications. Thus, the Polycarbonate –Carbon Dots composites are most well suited due to their high optical transparency and their ability to produce high quality thin films and various shaped monoliths. Their preparation and characterization are detailed in our published research papers [1,2]. These composites could be successfully implemented in high efficiency lighting devices.

Also their characteristics may offer a straightforward and cheap solution for solar UV protection of various sensitive surfaces provided by thin layers of prepared composites. One example is the protection of the painted surfaces or other sensitive parts (ex. automotive applications) long term exposed to direct sunlight by thin layers of composites containing PL efficient C-Dots. The protection is simply provided by the translation of solar UV radiation as excitation of the embedded C-Dots towards lower wavelengths, the lower energy photons (Stokes shift) produced in the radiative processes being markedly less harmful for the intended surface to be protected. From such a perspective, Carbon Dots are particularly suited due to their wide range UV excitation of the radiative processes, physico-chemical stability, inertness, lack of toxicity and ease of fabrication.

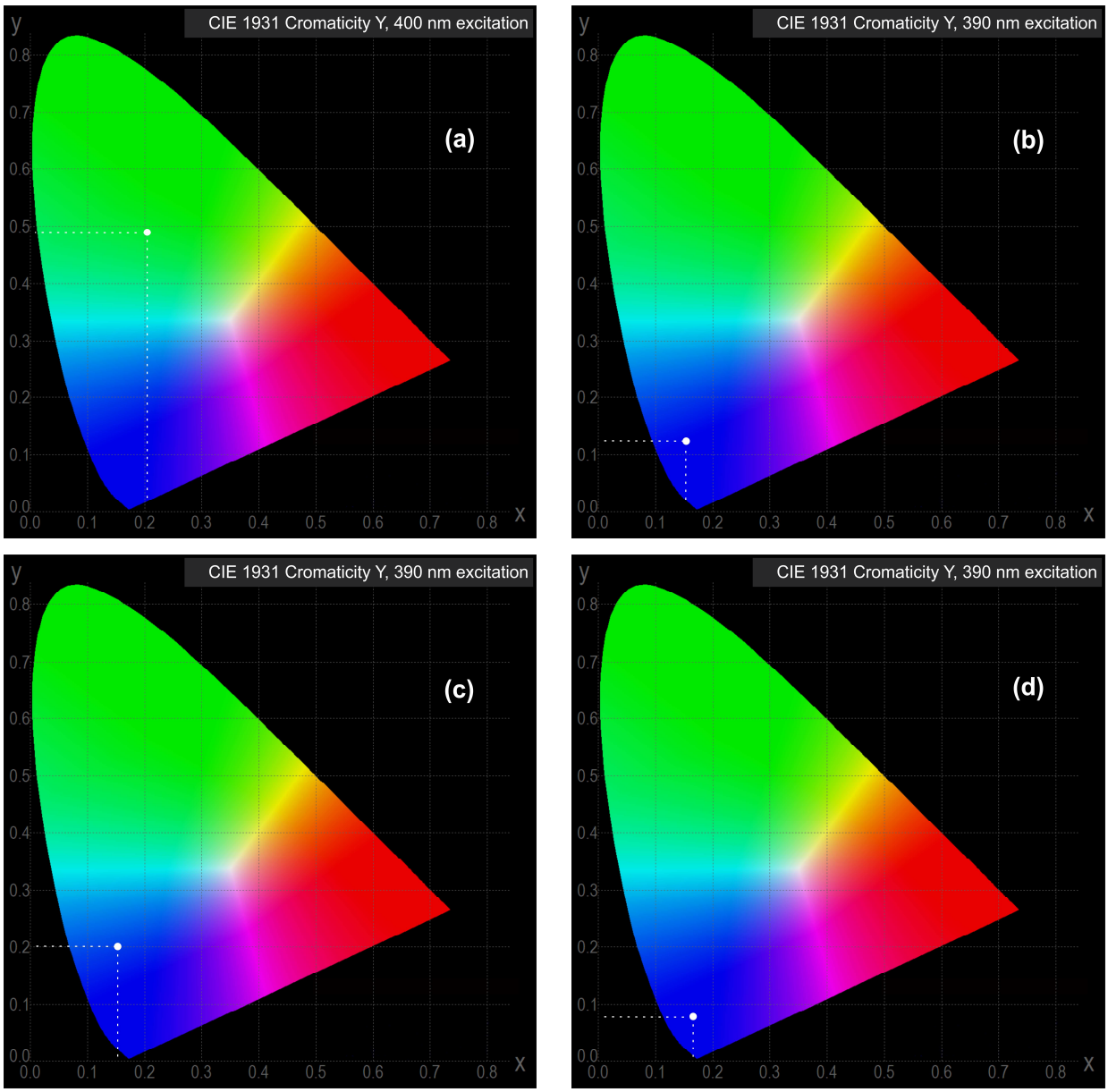

Figure 3. Chroma parameters according to CIE1931 recorded for Carbon Dots dispersed in (**a**) water, (**b**) acetone, (**c**) chloroform and (**d**) THF

The new composites with RGB emission described in our previous Scientific report (stage IV) are an interesting alternative for the backlighting system of the AMLCD displays which could provide several advantages over current solutions. The new possible implementation is presented in one of our published papers [3]. Besides the exposed advantages, the composites could be easily configured for this type of application due to their excellent ability to produce thin films using jet printing technique. Overall, our proposed approach could bring several advantages over the state of the art where composite polymer films including Quantum Dots are used (QD vision). The prepared RGB composites good be equally interesting for LED lighting sources, as photonic conversion mediums capable of producing fine tuned chromaticity attributes of the emitted light.

During the research activity within this research project the following scientif output was accomplished: **11** ISI published scientific papers in high ranked journals, with a cumulated impact factor over **25**, **1** ISI paper under review, **4** scientific papers lucrari in indexed journals, **2** patent requests and **10** participations at International Conferences. Also, **2** PhD theses were elaborated and successfully finalized within the scientific frame of the research project and under the in-depth scientific and experimental guidance of the research team members. The PhD theses were focused on RGB emissive compounds and materials and Carbon Dots.

Published ISI papers

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