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FELLOWSHIP FINAL REPORT

Carbon nanomaterials as solar UV protectors targeting applications ranging from paints/varnishes to pharma/cosmetic products

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ABSTRACT

The main goal of the project is the development of novel nanostructured carbon dots for their application as solar UV protectors in various materials, ranging from paints/varnishes to pharmaceutical/cosmetic products, which involve an entirely new approach in solar UV protection based on highly photoluminescent Carbon Dots (CDs) through efficient translation of the incident solar UV radiation towards longer wavelengths. The lower energy photons produced in the radiative processes within the CDs are less capable of inducing irreversible changes over the chemical/structural properties of the exposed surfaces. CDs are particularly suited for this approach due to their wide range UV excitation of the radiative processes, physico-chemical stability, inertness, lack of toxicity, biocompatibility and ease of fabrication. The provided UV protection is intended to be assayed upon their integration in various polymers matrices of relevance for coating materials and also targeting cosmetic skin UV protection formulations.

1- Introduction

Carbon Dots (CDs) are a new class of nanostructured materials that raises a growing scientific interest due to the remarkable properties such as: photoluminescent emission with high quantum yield (QY) conversion, lack of toxicity, high physical-chemical stability, resistance to photo-oxidation, facile surface functionalization, dispersibility in various solvents and facile preparation [1,2]. A remarkable feature of CDs is their intense photoluminescent emission characterized by emission peaks typically located in the range of 410-520 nm (blue-green) depending on the excitation radiation wavelength [3]. The wide spectral range of excitation is an extremely favorable feature for the targeted application and the radiative photoluminescent emission processes can achieve photonic conversion efficiency >75% [4]. The structural configuration of CDs consists in a defect rich graphitic core in 2-30 nm range, mainly composed of carbon atoms in sp^2 hybridization. Various terminal functional groups (-C=O, NH, COOH, -OH) are present within the graphitic structure or attached on the core surface, having an essential role in radiative photonic conversion processes [5,6]. This structure ensures a notable physico-chemical stability, thus allowing the use of CDs in various dispersion media such as organic solvents, monomers or polymers, which offers an outstanding advantage in the applications in the field of film materials. Another important advantage from the perspective of intended applications is the lack of toxicity [7,8].

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Common synthesis processes of CDs can be grouped as physical [9,10] and chemical methods, the latter being preferred due to the simplicity and quality of the resulting materials. The chemical processes namely consist in thermal treatment [11-13] or oxidation in acidic environments [14], in certain reported works the process being ultrasonic or microwave assisted [15]. Among them, the pyrolytic processing of the precursors might be seen as the most straightforward and technically unchallenging preparation method capable of yielding high quality CDs. Our recent studies on imide-derived CDs prepared through the pyrolytic approach are able to provide impressive PL emission [16-18] and also to easily alter their properties by doping with various transition metals [19]. Long term exposure of the varnishes/paints to the UV component of the incident solar radiation results in the irreversible degradation of the painted/ varnished surfaces, manifested as subtle changes of nuance, transparency degree, gloss or adhesion, due to structural changes of their polymeric component by the action of most energetic UV photons, which causes the breakdown of macromolecular chains, and the formation of oligomers or reactive species [20]. Hence, UV additives are essential for maintaining the characteristics of film materials from the category of paints and varnishes [21,22]. In this context, our approach of using CDs as UV protectors could be an effective, low cost and sustainable solution for UV protection as alternative to classic stabilizers.

2- Experimental details

The starting experimental activities were focused to further extend the author's previously developed N-Hydroxyphthalimide (NHF) derived Carbon Dots [17] to the intended use as UV protectors. One intended approach was the development of transition metals doped Carbon Dots. Therefore, the experimental studies were focused on obtaining NHF derived Carbon Dots doped with Cu(II), Co(II), Zr(IV) and Fe(II). In order to achieve this goal, the experimental studies involved in the first step the preparation of the NHF complexes with the above mentioned cations. The complexation reactions undergoes as follows:

$$xC_8H_5NO_3 + MCl_y \rightarrow [M(C_8H_4NO_3)_x(H_2O)] + yHCl$$

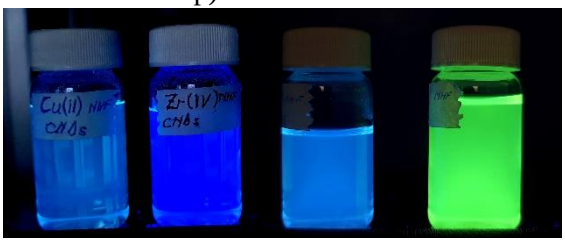
where M= Co(II), Cu(II), Fe(II), Zr(IV)

The NHF ligand is dissolved under stirring in a water-EtOH mixture (60/40% volume), while the Cu(II), Co(II), Zr(IV) or Fe(II) chloride was solved in water in a separate recipient. The complexation reaction commences through the mixing of the ligand and chloride solutions according to each case metal/ligand combination ratios (1/2 for Cu(II), Co(II), Fe(II) complexes and 1/4 for Zr(IV) complex). The reaction undergoes under stirring, at 40-45°C, for 24 hours in a simple laboratory setup, as illustrated below. The complex is obtained as a

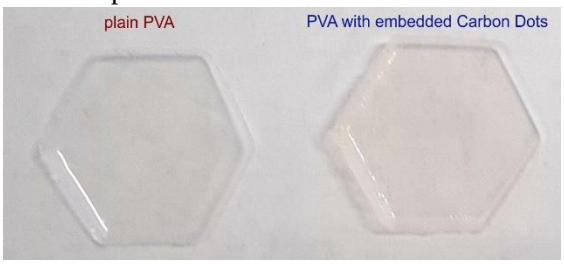
precipitate which is further 3 times washed with high purity water to eliminate the byproducts or unreacted precursors. Then, the prepared complex is dried 48 hours under vacuum at 70-75°C. The Cu(II), Co(II), Zr(IV) or Fe(II) doped Carbon Dots are further prepared through partial pyrolysis under controlled parameters (temperature, thermal exposure time of the precursors, etc) of the ante-prepared complexes. The laboratory setup used for the pyrolytic processing of the complexes is presented in the image below and it mainly consists of a quartz

tube able to withstand high temperatures and rapid cooling of the reaction mass through flooding with water, a surrounding glass mantle

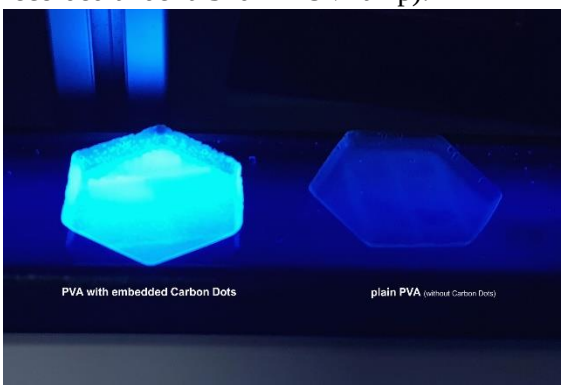
which maintain the hot heated air around the quartz tube and a temperature/flow regulated hot air source (50 - 650 ºC/ 150 - 500 l/min.).
Typically, the procedure of Carbon Dots preparation involve several stages, as follows: First, 0,2-0,3 g of the previously prepared NHF complex is added in the pyrolysis quartz tube; in the second stage, the hot air source is started (600ºC) at an air flow of 200 l/min. and after 1 min. it is raised to 500 l/min. and this thermal/flow regime is kept for 15 min; After this thermal exposure stage, the hot air source is stopped and the resulted reaction mass is quickly flooded with 10-15 ml cold water (4-5ºC); This primary aqueous dispersion containing Carbon Dots and chunks of residues is removed from the quartz tube and centrifugated in two stages (5000 RPM in first stage and 9000-10000 RPM in second stage); After first stage, the supernatant is collected and centrifuged again. After the second centrifugation stage, the supernatant is collected. The collected supernatant with a clear and slightly tinted aspect contains dimensionally selected doped Carbon Dots. In case other solvents must be used, it is required a supplementary operation involving the freeze drying of the aqueous dispersion. The obtained fine powder of Carbon Dots could be re-dispersed in various solvents according to the intended application. Depending on the cation (Cu(II), Co(II), Zr(IV) or Fe(II)) the fluorescent emission is ranging from blue to green, as illustrated in the picture below (recorded under 370 nm UV lamp).



In order to evaluate the UV protection provided by Carbon Dots they were embedded in the following polymer matrices : Polyacrylic acid, Polycaprolactone, Hydroxy ethyl cellulose, Hydroxy propyl cellulose, Poly vinyl alcohol, Polystyrene ; Poly vinyl chloride, Xantan gum.
In case of water soluble polymers the matrices were loaded by addition under vigorous stirring/moderate heating within the previously prepared aqueous dispersion of Carbon Dots, while in case of PS and PVC the Carbon Dots were first obtained in dry form and then re-dispersed in chloroform. As a typical procedure, the polymer (powder or pellets) is dissolved in the Carbon Dots dispersion (water or chloroform) and then processed in films or bulk. The influence of the Carbon Dots over the polymer matrices is minimal, as could be noted from the picture below.



The prepared polymer- Carbon Dots composites retain the photo-luminescent properties and characteristic emission of the embedded Carbon Dots, as illustrated below (the picture was recorded under a 370 nm UV lamp).



As could be noted, the PVA-Carbon Dots composite present a strong photo-luminescence located in the blue region of the visible spectrum compared with the plain PVA sample. The long term UV ageing tests were started using an UV-C source but, unable to be finished due to the premature stopping (end of April 2022) of the research project.

3- Results and discussion

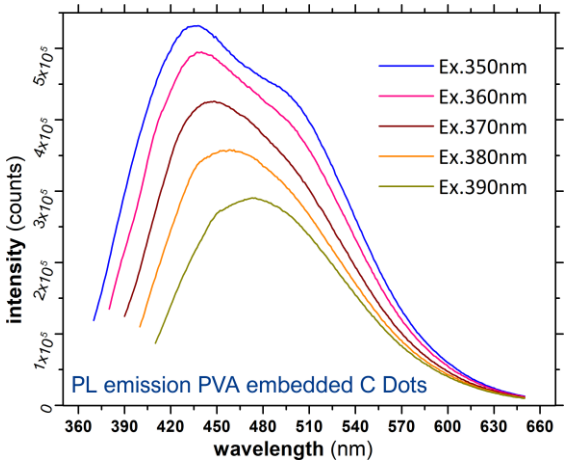
While the results are incomplete due to the premature ending of the research project, there are certain notable results, as following:
1. The prepared doped Carbon Dots present impressive photo-luminescent properties which

could be further investigated and adapted to an wider area of applications.

2. During the experimental work it was found that in case of liquid monomers (for example 2-hydroxy ethyl methacrylate, ethyl, butyl, hexyl acrylates, etc) it is possible to use a straightforward approach where the monomer is used directly after the final stage of the pyrolytic processing of NHF complexes, in order to obtain the primary dispersion. Therefore instead of using water, the cooled (5-10^{o}C) monomer is used to flood the reaction mass and to obtain the primary dispersion. Then, the procedure is according with that which was mentioned above. This experimental finding is very important because allows a direct dispersion of Carbon Dots without the necessity to disperse them in water (or other solvent, through freeze drying and re-dispersion) and then to dissolve the polymer. Also, using this approach is very useful in case of polymers which can not be dissolved in water or in case a crosslinked polymer is intended to be prepared. The liquid monomer Carbon Dots dispersion could easily be photo-polymerized to obtain highly photo-luminescent polymers processed in bulk, films and even nano/micro particles.

3. One major difficulty when using the Carbon Dots dispersions resulted from the pyrolytic processing (as described above) is the precise quantity determination of the Carbon Dots content within the dispersion (water or any other dispersion medium *e.g*. solvents or liquid monomers). Due to their morpho-structural particularities and even more important, due to very low quantities, traditional methods are not suitable or not able to provide enough measurement precision. In this view, during the research program, a new approach was defined and preliminary tested with very promising results. The approach is based on using QCM (Quartz Crystal Microbalance) adapted for measurement of Carbon Dots content in very low concentration dispersion, as resulting from the pyrolytic processing. While the experimental protocols where completed and successful measurements were recorded, the method still require further investigations which are currently in progress through co-operation with Prof. Vautrin-UI (Univ. D'Orleans).

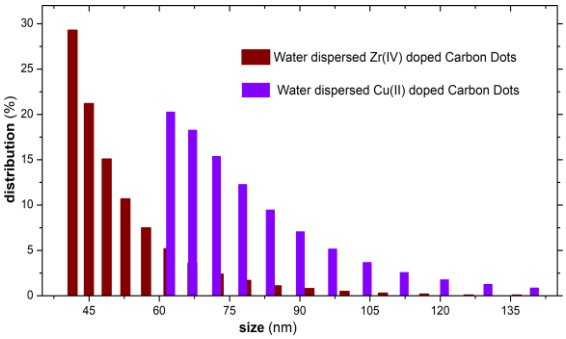
4. The photo-luminescence (PL) properties of the polymer embedded Carbon Dots were investigated. The results are typical for these type of carbon nanostructures with their excitation wavelength dependent emission peaks. Such behavior is often reported but, the exact PL mechanism is still an open debate subject. In certain studies [23] the quantum confinement effect is considered to be responsible for the PL properties in a similar approach to the "classic" semiconductor quantum dots, while other opinions tend to emphasize the role of surface functional groups in achieving the excited states responsible for the excitation wavelength-dependent emission [24]. In the following graph is presented the PL emission of the Zr(IV) doped Carbon Dots embedded in the PVA matrix.



The emission peaks are excitation dependent as detailed in the following table:

Ex(nm)	350	360	370	380	390
Em.Peak (nm)	438	440	448	458	473

5. The dimensional analysis (DLS) revealed certain differences among the Carbon Dots doped with Cu(II) and Zr(IV) cations, as presented in the figure below:



In case of the Zr(IV) doped Carbon Dots the average dimensions are situated within the 40-60 nm range while in case of the Cu(II) doped Carbon Dots the average dimensions are within 60-80 nm range. It is known that Carbon Dots present a pronounced clusterization tendency, therefore the results of the DLS investigation are most likely to provide a size distribution of the clusters and not of the Carbon Dots individual units. This unwanted agglomeration tendency negatively affect the PL emission, therefore it is advised to use freshly prepared Carbon Dots dispersions for further introduction in the polymer matrices.

4- Conclusion

While the associated research program was prematurely interrupted due to a certain unavoidable situation, the results achieved within the limited period of implementation could be summarized as follows: Synthesis and partial characterization of new Co(II), Cu(II), Fe(II), Zr(IV) doped Carbon Dots through pyrolysis of NHF complexes with ante-mentioned cations. All prepared Carbon Dots present characteristic photo-luminescence; A new approach was successfully tested and demonstrated to directly use certain monomers (for example 2-hydroxy ethyl methacrylate, ethyl, butyl, hexyl acrylates, etc) as dispersion mediums in the next stage after the thermal processing. This approach avoids the intermediary stages of aqueous dispersion, freeze drying and redispersion in suitable solvents for polymers which are not water soluble. Instead of using water, the cooled (5-10^{o}C) monomer is used to flood the reaction mass and to obtain the primary dispersion.The direct introduction of Carbon Dots in monomers leads to an straightforward route to obtain polymers with embedded Carbon Dots and extend the types of polymers which could be potentially used or where a crosslinked polymer is intended to be prepared. The new approach is particularly useful for obtaining polymer-Carbon Dots composites (thin films, bulk or nano/microparticles) through photo initiated polymerization. Using this new approach, new types of coatings providing solar UV protection could be obtained; Also, the determination of the Carbon Dots content within their dispersions in various solvents resulted after the pyrolytic preparation, was investigated using a new approach. As the conventional methods are not suitable or not expected to provide accurate measurements, a new method was taken into consideration which uses a QCM equipment (Quartz Crystal Microbalance). The measurement protocol was adapted to the prepared dispersions of Carbon Dots within the constraints of the QCM method. This approach is currently under experimental investigation, so far the results being very promising. Using the QCM method is particularly important in case of new pharma/ cosmetic formulations based on Carbon Dots.

5- Perspectives of future collaborations with the host laboratory

Despite the project was interrupted, within the limited period of development an in-depth cooperation was established. One very important direction is a research project developed with Dr.Ania Conchi within the framework of LEAP-RE Horizon 2020 EU-funded project. The project was submitted and successfully accepted for financing, being currently in progress. It is a consortium with France as coordinator (dr. Ania, CEMHTI, as consortium leader), TUIasi University Romania as main partner (also financially supported by UEFISCDI Ro, C.Stan as coordinator) and Maroc, Algeria and Egypt as African partners. The main goal of the project is developing new materials based on Carbon Dots and coordination polymers for enhancing the conversion efficiency of the solar photovoltaic cells. Another important achievement already accomplished is a new ERASMUS cooperation

agreement between University of Orleans and University TUIasi Ro. Due to author's initiative and involvement, the program is already operational, started from 1st October 2022. There are also multiple research directions in progress with scientists from CEMHTI or University of Orleans. The new method of Carbon Dots content in dispersions using QCM technique is currently under development with Prof. Christine Vautrin-UI with which also new types of photo-emissive polymers are intended to be studied and developed. The studies regarding Carbon Dots in polymer matrices for UV protection are continued through a close co-operation with Dr.Ania and other researchers from CEMHTI. There is a strong commitment for some new research project proposals to be submitted to future open competitions within European Research framework. The main directions are focused on polymer materials for hydrogen storage, luminescent materials based on Carbon Dots and cosmetic formulations for skin UV protection based on new developed Carbon Dots and polymer composites.

6- Articles published in the framework of the fellowship

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2. Corneliu S. STAN, Hiba IDRISSI, Guido PERRIN, Conchi O. ANIA, Imide-derived carbon nanodots, a promising new approach as UV protectors, Carbon 2022, The World Conference on Carbon 3-8 July, Imperial College London UK.

7- Acknowledgements

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