AIDIC EFCE
ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Fluorescent carbon nanodots formation in laminar flames

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Highlights

- Fluorescent carbon nanoparticles
- Carbon dots from controlled combustion
- Fuel-rich combustion: a direct source of fluorescing carbon nanodots that do not need to be passivated to become photoactive.

1. Introduction

Carbon dots emitting visible fluorescence are the emerging materials which have been recently added to the big family of carbon materials after their discovery in 2004 in arc discharge soot [1]. They are considered as cheaper and health friendly substitutes of inorganic nanostructures currently featuring quantum nanodots. Laser ablation plasma, chemical vapor deposition processes followed by laboratory treatment with oxidation agents are the main sources of carbon dots. Research is currently very active in discovering alternative sources. Combustion in fuel-rich, i.e. pyrolytic, conditions is a known source of strongly fluorescing molecules as polycyclic aromatic hydrocarbons (PAH). In looking for higher molecular weight species and/or particles involved in soot formation, green-fluorescing species have been for the first time detected in the raw soot particles [2]. Thereafter, simple combustion systems like candles have been found as source of carbon nanodots precursors [3].
In view of a possible exploitation of fuel-rich combustion as a convenient and tunable source of quantum carbon nanodots, this work presents insights in the spectroscopic (absorption and fluorescence) properties of fluorescing carbon which accompanies soot formation in laminar flames.

2. Methods

Flame-formed carbon particulate matter was sampled in an ethylene laminar flame and extracted with dichloromethane (DCM) and N-Methyl-pyrrolidone (NMP) getting blue-violet fluorescent carbon and green fluorescent carbon, respectively. It is worth to note that such carbon materials were insoluble in water suggesting the low presence of oxygen functionalities. Absorption and fluorescence spectra of the samples are necessary for determining the excitation and observation wavelengths. The linear absorption spectra of the samples were recorded on a diode array spectrophotometer (HP8453) in the wavelength range 260–800 nm. The steady-state fluorescence spectra have been recorded with a spectrofluorometer (Perkin-Elmer LS-50) in the 220-700 nm wavelength range.

3. Results and discussion

The absorption and synchronous fluorescence spectra of the blue-violet and green fluorescent carbon are reported in Figs. 1a and 1b. The absorption maximum of the blue-violet fluorescent carbon extracted with DCM from soot (Fig. 1a) corresponds to the maximum excitation wavelength (250nm) as shown in Fig. 1c where excitation and emission spectra of the blue-violet fluorescing carbon are contrasted. This spectral feature, along with the fine structure of synchronous and emission spectra and the high quantum efficiency measured (10^{-1}), is consistent with a distribution of PAH molecules in the mass range of 100–800 u [2, 4-5].
The green fluorescence is own of the species extracted from soot with a powerful solvent as NMP. The absorption spectrum is broader and extended into the visible in respect to the blue-violet fluorescent carbon (Fig. 1a). Moreover, the green-fluorescing carbon presented a lower quantum efficiency (10^{-2}-10^{-3}) [2]. The maximum of the excitation spectrum is largely shifted into the visible (400nm) in respect to the UV absorption maximum (<250nm) (Fig. 1d). This difference suggests the higher complexity of the green-

fluorescing carbon featured by the presence of non-emitting and emitting chromophores. If these different chromophores are associated to a unique carbon network is verified by looking at synchronous spectra (Fig. 1b) and the time-resolved fluorescence polarization anisotropy (TRFPA) measures (Fig. 1e). The diameter of the fluorescing particles obtained from the TRFPA rotational time [4,5] was measured in previous work to be around 1-3nm [4-5]. Actually, the synchronous spectrum of the green-fluorescent carbon shows a broad feature as opposed to the fine structure exhibited by the blue-fluorescing carbon, confirming the hypothesis of a unique big molecule and/or particle making up the green-fluorescent carbon. The absence of a correlation between the TRFPA diameter, reported on the ordinate of Fig. 1e, and the chromophore size related to the emission wavelength reported in the abscissa of Fig. 1e indicates that the green-fluorescent carbon is composed of chromophores (4–8 aromatic rings) emitting in the 350-600nm range bonded together in a sort of archipelago structure, or attached to a carbon network with average 1-2 nm size.

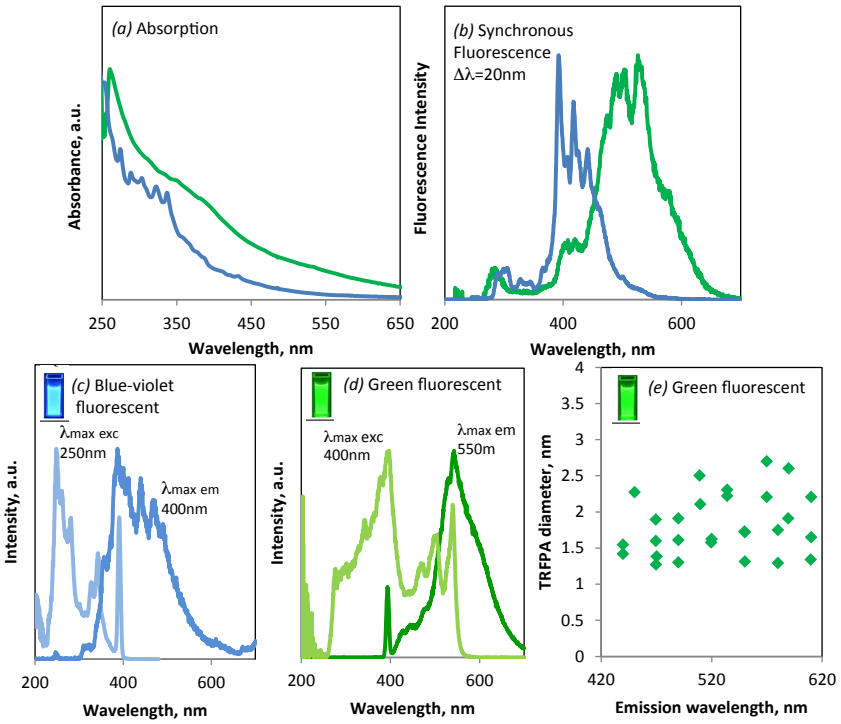

Figure 1. Absorption spectra (a), synchronous fluorescence spectra (b), excitation and emission spectra of blue-violet (c) and green-fluorescing carbon, (d) extracted from a typical ethylene flame soot sample; TRFPA diameter of green fluorescent carbon [4-5] (e).

4. Conclusions

In comparison with current production technologies, the fuel-rich combustion showed to be a direct source of fluorescing carbon nanodots that do not need to be passivated to become photoactive. By using different solvents, blue-violet and green fluorescing carbon, promising for preparing carbon nanodots, were easily separated and spectroscopically characterized.

References

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Keywords
Carbon nanodots, fluorescent carbon, spectroscopy

Carmela Russo Short Curriculum Vitae

PERSONAL INFORMATION

Family name, First name: Russo, Carmela

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Date of birth: 19/12/1984

Nationality: Italian

• EDUCATION

2013 PhD at the Chemical Engineering Department, University of Naples Federico II, Italy. Supervisor: Professor Andrea D'Anna

2009 Master in Chemical Engineering, Grade: 110/110 cum laude, University of Naples Federico II, Italy.

• CURRENT POSITION

2016 – Fixed Term Researcher
Istituto di Ricerche sulla Combustione, CNR, Italy.

• PREVIOUS POSITIONS

2014 – 2016 Postdoctoral Researcher
Istituto di Ricerche sulla Combustione, CNR, Italy.

2014 – 2013 Research assistant in Naples at Cons. Naz. Interuniv. Scienze Fisiche della Materia (CNISM).

• AWARDS AND FELLOWSHIPS

2015 Winner of the "Ricercatamente" Prize as the best young researcher of CNR for the Department of Engineering, ICT and Energy and Transport Technologies (DIITET). The award was sponsored by the National Research Council of Italy and Accademia Nazionale dei Lincei.

2014 Winner of the Bernard Lewis Fellowship of The Combustion Institute assigned to the five best young researchers in the field "to encourage high quality research in combustion by young scientists and engineers". The award was sponsored by The Combustion Institute.

2014 Winner of a Grant as Visiting scientist (1 week) at Trieste for performing carbon analysis by synchrotron radiation (Project proposal #20135066 supported by Elettra - Sincrotrone Trieste S.C.p.A. ; Resp.: Dr. B. Apicella).

2013 – 2011 Winner of No. 3 grants from European project COST Action CM0901 as presenter to the COST conferences in Zaragoza, Perugia and Sorrento.

2012 Winner of a PhD scholarship (7 months) from Ministero dell'Istruzione dell'Università e della Ricerca (MIUR) as visiting PhD student at Cambridge University (UK).

2012 Winner of a Grant as PhD student presenter at the 34th International Symposium on Combustion sponsored by The Combustion Institute .

2013 – 2010 Winner of a PhD scholarship from Ministero dell'Istruzione dell'Università e della Ricerca (MIUR)

• SUPERVISION OF GRADUATE STUDENTS

2011 – Co-supervisor of 4 M.S. research projects (Elisabetta Cepollaro, Lucia Giarracca (now PhD student at University of Lille, Lucio Taddeo (now PhD student at National Institute of Applied Sciences) and Nicol Sferragatta) and 3 B.S. research projects (Nicola Zalloni,

Lucia Giarracca, Lucio Taddeo and Giuseppe Sdanghi) at the Chemical Engineering Department of University of Naples Federico II.

- **TEACHING ACTIVITIES**

2011 – Lecturer for M.S. courses of Environmental Chemical Engineering (6h/year) and of Combustion (6h/year) at the Chemical Engineering Department of University of Naples Federico II.

- **ORGANISATION OF SCIENTIFIC MEETINGS**

2017 Charman at the XXXX Meeting of the Italian Section of the Combustion Institute on SOOT, NANOPARTICLES, PAH AND OTHER LARGE MOLECULES colloquium.

- **INSTITUTIONAL RESPONSIBILITIES**

2013 – 2010 Member of the Faculty Committee of the Chemical Engineering Department of University of Naples "Federico II" as Representative of PhD students of the Chemical Engineering Department of University of Naples Federico II.

- **COMMISSIONS OF TRUST**

2014 – Reviewer for peer-reviewed international congresses and scientific journals: Combustion and Flame, Fuel and Proceedings of the International Combustion Institute.

- **MEMBERSHIPS OF SCIENTIFIC SOCIETIES**

2010 – Member of the International Combustion Institute.
2010 – Member of the Italian Section of the Combustion Institute.

- **MAJOR COLLABORATIONS**

Prof. Angela Amoresano, University of Naples Federico II, on Time of Flight Mass Spectrometry of complex carbonaceous materials.
Prof. Andrea Carlo Ferrari, University of Cambridge (UK), on Raman spectroscopy of graphene-based carbon materials.
Dr. Mario Iodice, Istituto per la Microelettronica e Microsistemi-CNR, on structural characterization of photodetectors and electronic devices based on erbium and graphene.
Prof. Joann S. Lighty, Boise State University (USA) for structural characterization of particulate formed in inverse diffusion flame
Dr. Vito Mennella, Istituto Nazionale di Astrofisica, on synthesis and structural charaterization of thermally treated pitches and carbon materials.
Prof. Marcos Millan, Imperial College (Dept. of Chemical Engineering) of London (UK), on chemical characterization of pitch materials analogous to combustion-formed condensed phases.
Prof. Pascaline Pré, CNRS unit GEPEA of Nantes (France), on HR-TEM measurements for soot particles nanoscale characterization.
Prof. J-N. Rouzaud, Laboratoire de Géologie de l'Ecole Normale Supérieure, CNRS-ENS of Paris (France), on HR-TEM measurements for soot particles nanoscale characterization.
Prof. Viktor Scherer, University of Bochum (Germany), on coal pyrolysis and transformation in a drop tube reactor.
Prof. Randy Vander Wal, Penn State University (USA), on HR-TEM measurements on soot particle and annealed carbonaceous particulates.

- **CAREER BREAKS**

22/11/2016-24/04/2017 maternity leave of 6 months for the birth of my daughter (24th December 2016).

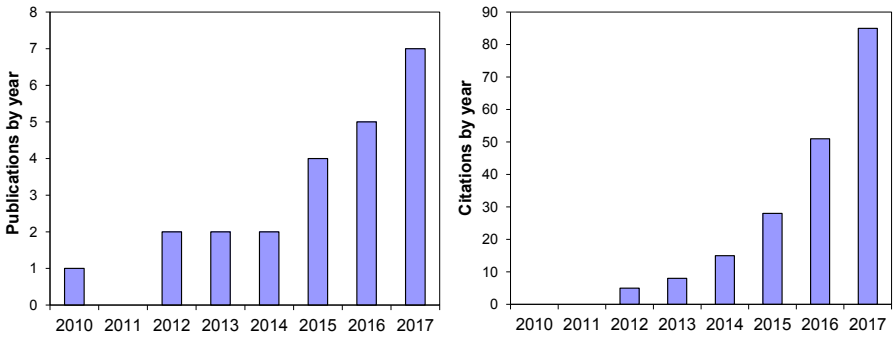
- **SCIENTIFIC PRODUCTION**

My main research topics are:

✓ Monitoring, control, and study of the energy efficiency and environmental impact of combustion-based energy production systems;

✓ Advanced diagnostics for characterization of materials relevant to energy and environment;

✓ Production of carbon materials relevant to environmental and energy fields.



During my carrier I have published 23 peer-reviewed journal articles, including 11 as first author, 10 as first and corresponding author, 9 as last author, 3 as a coauthor. Total citations No. 193, H-index 9 @Nov. 2017 source Scopus. A resume of my output is reported in the slide. 4 of these works have been presented at the International Symposium on Combustion, the top international conference in the combustion field, and issued in the related Proceedings of the Combustion Institute (I.F. 2016: 3.214). The majority of my papers have been published on top journal in the combustion and energy field (4 on Combustion and Flame I.F. 3.663, 3 on Energy and Fuel I.F. 3.091, 2 on Fuel I.F. 4.601). However, just thanks to the acquired experience on the development of spectroscopic tools, as effective methods for the structural characterization of carbonaceous materials I was able to expand my research interests beyond the combustion and clean energy fields and to publish two papers on Carbon (I.F. 6.337) a journal for communicating scientific advances in the field of carbon materials. I published papers with 26 different coauthors, coming from 10 different institutions, most of them (7) international, testifying the worldwide relevance of my research activity. I was oral presenter of 18 contributions to international/national conferences. The awards "Ricercatamente" from CNR (2015) and the Bernard Lewis Fellowship from the International Combustion Institute (2014) testify the research community appreciation to my achievements. From a didactic point of view, I have supervised the final MS projects of several students at the chemical engineering department of the University of Naples Federico II, with direct responsibilities on his formation and research activities, infusing a professional but above all enthusiastic approach to this job. Two of them now are doing their own PhD in France.

- **PROJECTS**

Project	***Period***	***Role of candidate***
Oxyflame project SFB/TR 129 supported by German Science Foundation	01/09/2015 to date	**Partecipant**
"Miglioramento dell'efficienza energetica dei sistemi di conversione locale di energia" PAR 2013/2014 supported by Accordo Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche	01/04/2014 – 31/01/ 2016	**Partecipant**
"Utilizzo pulito dei combustibili fossili ai fini del risparmio energetico" PAR 2011/2012 supported by Accordo Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche	01/01/2012 – 31/03/2014	**Partecipant**
"Integrazione della tecnologia MILD in sistemi innovativi di combustione a basso impatto ambientale" INDUSTRIA 2015 supported by Ministero per lo Sviluppo Economico (MiSE).	01/01/2009– 31/12/ 2013	**Partecipant**
"Valutazione ed utilizzazione dei biocombustibili ottenuti da residui o scarti agricoli di scarso valore intrinseco e di alghe per l'applicazione in impianti di cogenerazione su microturbine" PAR	01/01/2011– 31/12/ 2011	**Partecipant**

2011/2013 supported by Accordo di Programma tra il Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche.		
"Carbone pulito-CO2 capture" PAR 2009/2011 supported by Accordo di Programma tra il Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche..	01/01/2011– 31/12/ 2012	**Partecipant**
"Metodologie innovative di sviluppo di motopropulsori automobilistici" PON2011.	01/01/2011 - 31/12/2014	**Partecipant**
"Polveri ultrafini ed effetti sulla salute". PRIN2008	22/03/2010 - 22/09/2012	**Partecipant**
"Carbone pulito-CO2 capture" PAR 2009/2011 supported by Accordo di Programma tra il Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche.	01/01/2010– 31/12/ 2010	**Partecipant**
"Carbone pulito-CO2 capture" PAR 2009/2011 supported by Accordo di Programma tra il Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche.	01/01/2009– 31/12/ 2009	**Partecipant**
"Studio dell'effetto delle caratteristiche chimiche del combustibile sulla formazione di prodotti di ossidazione e del particolato" by ENI Tecnologie/IRC-CNR 2008 N. 4900169892.	01/01/2008 - 30/03/2009	**Partecipant**
"Carbone pulito" supported Accordo di Programma tra il Ministero dello Sviluppo Economico e il Consiglio Nazionale delle Ricerche.	01/01/2008– 31/12/ 2008	**Partecipant**