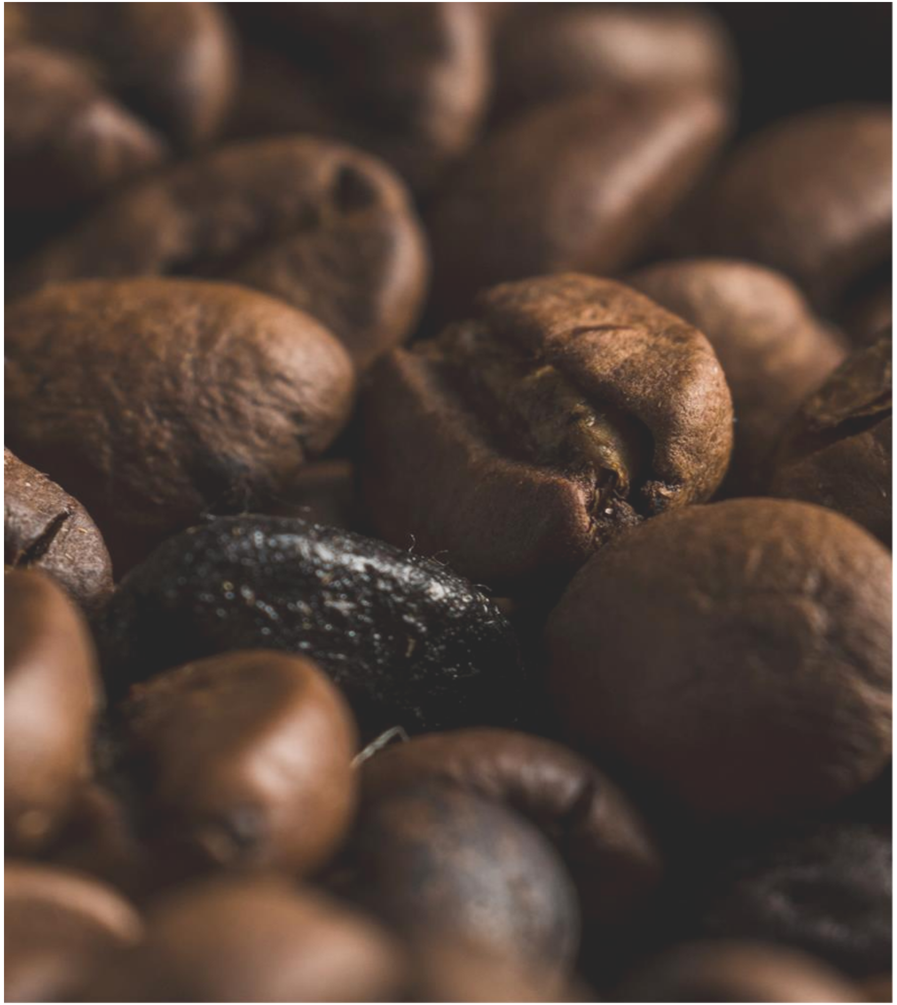

Carbon Dots Synthesis from Coffee Grounds, and Sensing of Nitroanilines

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OBJECTIVES

- Synthesis of carbon dots (C-dots) from coffee grounds (CGs) produced from automatic machines using a sustainable and ecofriendly one-pot microwave-assisted hydrothermal carbonization (Mw-HTC) procedure;
- Structural and photophysical properties of C-dots using FTIR, ^{1}H NMR, UV-Vis, and fluorescence techniques;
- Evaluation of the sensorial ability of the as-synthesized C-dots toward isomeric nitroanilines through fluorimetric titration experiments.

1. INTRODUCTION

C-dots

Carbon-based nanomaterials that have attracted the researchers interest due their excellent luminescence, photostability and biocompatibility, encouraging their use in several fields such as biomedicine, sensing, (photo)catalysis and optoelectronics.[1-5]

Production and Source

Top-down and bottom-up methods using a great diversity of carbon sources, namely several types of wastes, either from industrial or forest origin.[2-4,6-8]

Coffee

One of the most consumed brews all over the world, generating large amounts of waste with high content of organic matter such as caffeine, phenols, tannins, and sugars in it.[9]

Coffee Waste

To reduce such an environmental impact of this ubiquitous residue, research has been undertaken to convert CGs into high-added value products.[9,10]

2. RESULTS AND DISCUSSION

01. Synthesis

- Fluorescent C-dots were synthesized from CGs in an eco-friendly way using Mw-HTC procedure;
- The effect of the residence time on the C-dots luminescence, keeping constant the reaction temperature and the amount of additive were evaluated (Table 1).

Table 1. Time effect on fluorescence quantum yield and mass yields.[1]

Entry	Time (h)	Φ_F (λ = 380 nm)	Mass (%)
1	1	0.062	17.01
2	2	0.087	16.23
3	3	0.098	16.90
4	4	0.087	9.67
5[2]	3	0.032	11.96

[1]Typical reaction conditions: CGs (154 mg), ED (27µL), 190 °C, 18 bar, stirring and N_2; [2]Urea (24.3 mg) as additive.

- The highest luminescent nanomaterials were obtained upon 3h of irradiation;
- The nature of the nitrogen-rich additive showed a relevant impact on the fluorescence quantum yield.

2. RESULTS AND DISCUSSION

02. Structural Characterization

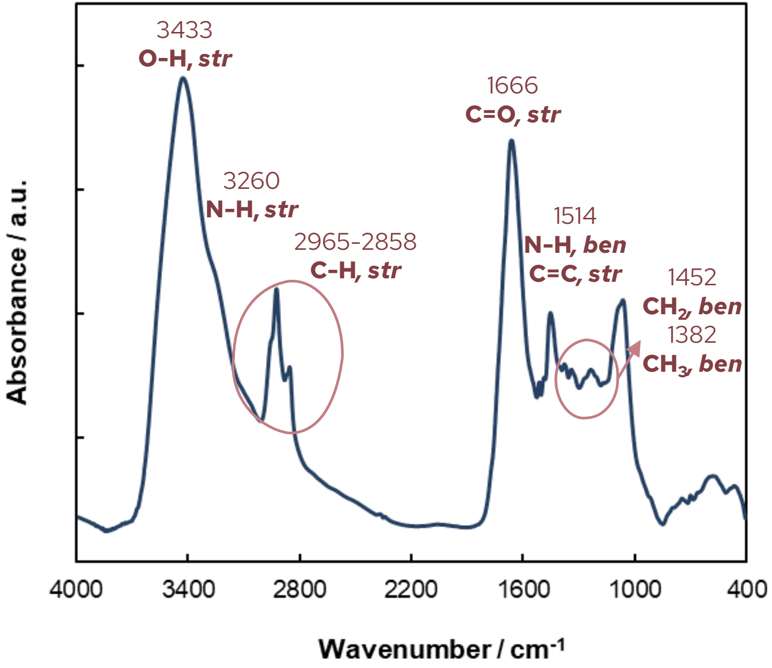

Figure 1. FTIR spectrum (KBr) of C-dots.

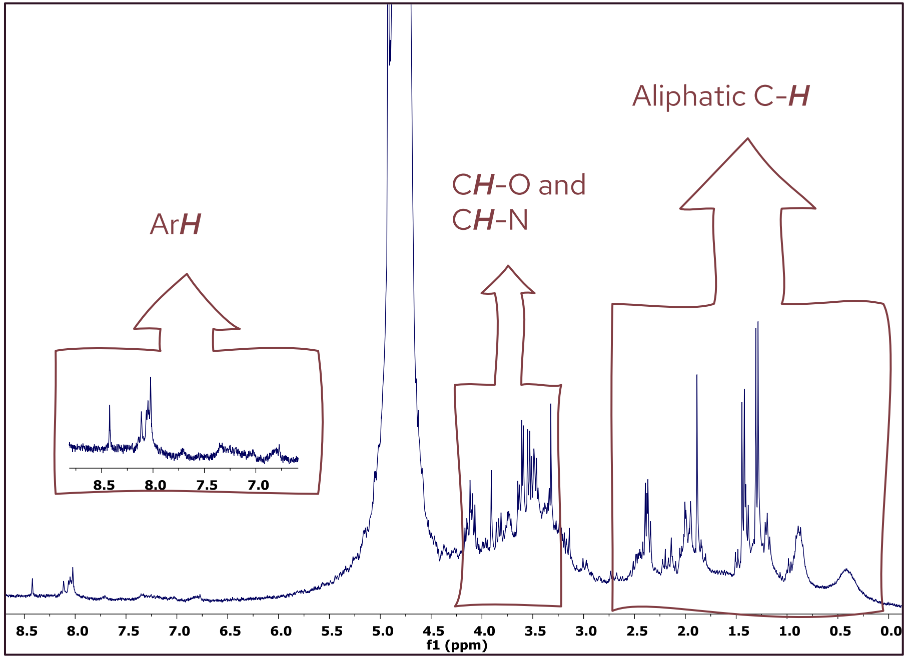

Figure 2. ^1H NMR spectrum of C-dots in D_2O.

2. RESULTS AND DISCUSSION

03. Photophysical Properties

- Studied by UV-Vis and fluorescence spectroscopies.

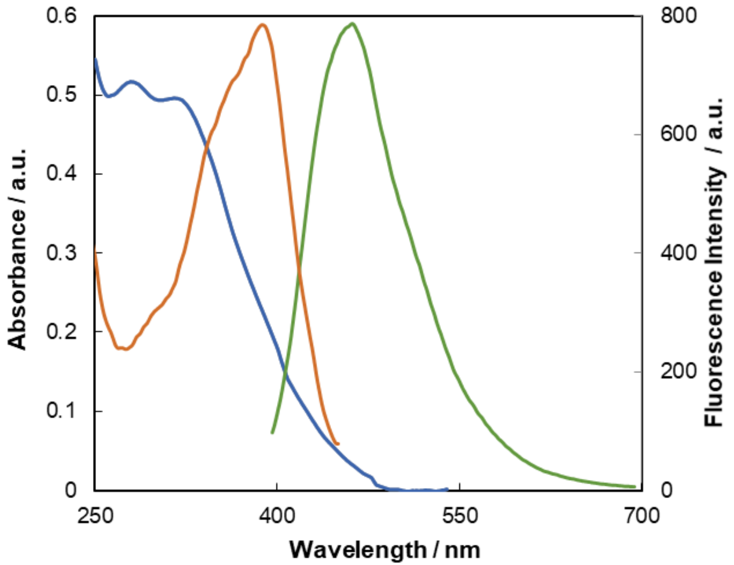

Figure 3. UV-Vis (blue line), excitation (orange; monitored at 462 nm) and emission (green line; λ_{exc} = 380 nm) spectra of aqueous dispersions (0.1 mg/mL).

SPECTRA

- **Absorption** ➡ bands peaking at ***ca.*** 285 nm and 325 nm, with a shoulder near 400 nm;
- **Excitation** ➡ main chromophores responsible for the emission appear at around 300, 348 and 392 nm.
- **Emission** ➡ band with maximum at 462 nm, when excited at 380 nm.

2. RESULTS AND DISCUSSION

04. Detection of Nitroanilines by C-dots

- Application of C-dots as sensing materials for NAs was evaluated by fluorescence and absorption techniques.
- The reduction in fluorescence emission intensity was quantified by the Stern-Volmer equation and correction for h-IFEs was applied at the excitation (380 nm) and emission wavelengths (462 nm)

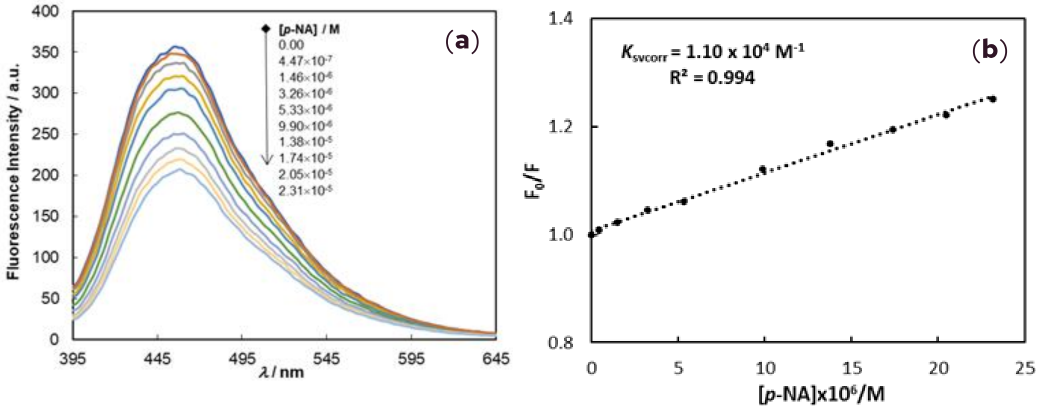

Figure 4. (**a**) Emission spectra of C-dots (0.01 mg/mL) after successive additions ($4.47x10^{-7}$-$2.31x10^{-5}$ M) of ***p***-NA (λ_{exc}=380 nm). (**b**) Stern-Volmer plot after correction for h-IFE.

Table 2. Stern-Volmer quenching constants of C-dots with NAs.[1]

Entry	Nitroaniline	K_{sv}/M^{-1}	$K_{sv\ corr}/M^{-1}$
1	***ortho***-NA	$1.40x10^4$ (R^2 = 0.998)	$7.09x10^3$ (R^2 = 0.999)
2	***meta***-NA	$3.62x10^3$ (R^2 = 0.985)	$2.16x10^3$ (R^2 = 0.976)
3	***para***-NA	$3.10x10^4$ (R^2 = 0.999)	$1.10x10^4$ (R^2 = 0.992)

[1]Excitation at λ = 380 nm in the concentration range (447 nM - 23.1 μM).

High sensitivity for *p*-NA

3. CONCLUSIONS

- CGs waste can be used as a suitable carbon source to produce fluorescent C-dots through sustainable one-pot Mw-HTC method;
- C-dots photophysical properties can be modulated by the experimental conditions (residence time, temperature, and additive nature) used in its synthesis;
- The highest luminescent carbon nano-materials were evaluated as sensors for isomeric nitroanilines detection ➡ a high selectivity and selectivity were attained for ***p***-NA;
- **These preliminary results revealed that CGs associated with Mw-HTC could provide an environmentally sustainable route for the synthesis of C-dots with useful practical applications.**

Acknowledgements

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