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Carbon Dots Synthesis from Coffee Grounds, and Sensing of Nitroanilines †

Bianca Moraes [1], Alexandra I. Costa [1,2,*], Patrícia D. Barata [1,2] and José V. Prata [1,2]

[1] Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal; email 1 (B.M.); email 2 (P.B.D.); email 3 (J.V.P.)
[2] Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal
* Correspondence: acosta@deq.isel.ipl.pt

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Abstract: Fluorescent carbon dots (C-dots) were directly synthesized by a sustainable and eco-friendly one-pot microwave-assisted hydrothermal carbonization method from coffee grounds waste. The coffee grounds obtained from automatic coffee machines, after being heated at 190 °C for 1–4 h in the presence of nitrogen additives, furnished the desired carbon nanomaterials. Structural and photophysical properties of the as-synthesized nanomaterials were evaluated by FTIR, ^{1}H NMR, UV-Vis, and fluorescence spectroscopies. The ability of the C-dots to behave as probes for isomeric nitroanilines (*ortho-*, *meta-* and *para-*nitroaniline) was explored through fluorimetric titration experiments. High sensitivities and selectivities were obtained for the detection of nitroanilines in aqueous media.

Keywords: carbon dots; coffee grounds; fluorescence; microwave; sensor; nitroanilines; pollutants

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1. Introduction

Carbon-based nanomaterials, particularly carbon dots (C-dots) 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].

C-dots can be prepared by a variety of methods (top-down and bottom-up approaches), using a great diversity of carbon sources [2]. Use of several types of wastes, either from industrial or forest origin, for C-dots production has been achieved [3,4,6–8]. Coffee is one of the most consumed brews all over the world, generating large amounts of waste. This represents a source of environmental problems due to the high content of organic matter such as caffeine, phenols, tannins, and sugars in it [9]. To reduce such an environmental impact of this ubiquitous residue, research has been undertaken to convert coffee grounds (CGs) into high-added value products [9,10].

Herein we report the first results concerning the synthesis of C-dots from CGs using a one-pot microwave-assisted hydrothermal carbonization (Mw-HTC) procedure. The structural and the photophysical properties were evaluated and the sensing ability of the as-synthesized C-dots toward isomeric nitroanilines detection was performed by fluorescence-based titrations experiments.

2. Materials and Methods

2.1. Instruments and Methods

FTIR spectra were obtained on a Bruker Vertex 70 as KBr pellets (transmission mode). Band assignments were made by indicating the nature of the vibration [stretching (str) and bending (ben)]. ^{1}H NMR spectra were collected on Bruker AVANCE II+ spectrometer

(300 MHz) at 25 °C using solutions or dispersions of C-dots in D_2O. The reported chemical shifts (δ/ppm) are referenced to residual solvent signal (4.790 ppm).

UV-Vis spectra were recorded on a VWR UV 3100PC or on a Jasco J-815 spectrophotometer at 20 °C using 1-cm quartz cells.

Steady-state fluorescence spectra were acquired on a Perkin Elmer LS45 fluorimeter using a 1-cm quartz cuvette in right angle (RA) geometry at 25 °C in air-equilibrated conditions.

Reactions under microwave irradiation were performed in a mono-mode microwave reactor (CEM, Discover), using pressure-rated reaction vials with poly(tetrafluoroethylene)-silicon caps.

Fluorescence quantum yields (Φ_F) were measured in aqueous solutions using quinine sulphate in 0.01 M H_2SO_4 ($\Phi_F = 0.54$; air equilibrated conditions, RA geometry) as reference standard at 25 °C [11]. To prevent inner filter effects during quantum yield measurements the optical density of the samples and reference were kept below 0.05 at the excitation wavelength. The quantum yields were calculated by the slope method, according to a reported procedure [12]. Fluorescence (emission and excitation) spectra were recorded with the same operating settings.

Sensing assays were performed with aqueous dispersions of C-dots (0.01 mg/mL) obtained under the conditions reported in Table 1, entry 3. Titration experiments were achieved at constant concentration of C-dots by adding known amounts of isomeric nitroanilines (NAs) (from 447 nM to 23.1 μM), being the spectra repeatedly acquired after each addition. After exciting at the desire wavelength ($\lambda_{exc} = 380$ nm), the maximum intensity of the fluorescence emission curves were taken to derive the sensitivity of the C-dots towards NAs making use of the Stern-Volmer equation $F_0/F = 1 + K_{SV}[Q]$, where F_0 and F are the fluorescence intensities of C-dots in the absence and presence of the quencher, [Q] is the quencher concentration and K_{SV} is the static Stern-Volmer constant [13].

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

Entry	Time (h)	Φ_F ($\lambda = 380$ nm)	η_{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 (27 μL), 190 °C, 18 bar, stirring and N_2. [2] Urea (24.3 mg) as additive.

The fluorescence intensities were corrected for hetero-inner-filter effects (h-IFEs) of the NAs at the excitation and emissions wavelengths using the expression: $\eta = (Ax_0{*}Ay_0{*}(1\text{-}10\text{^}(\text{-}Ax_i)){*}(1\text{-}10\text{^}(\text{-}Ay_i)))/(Ax_i{*}Ay_i{*}(1\text{-}10\text{^}(\text{-}Ax_0)){*}(1\text{-}10\text{^}(\text{-}Ay_0)))$, where Ax_0 and Ay_0 are the fluorophore absorbances and $Ax_i = Ax_0 + \Delta Ax_i$ and $Ay_i = Ay_0 + \Delta Ay_i$ are the total absorbances of the fluorophore and the quencher (ΔAx_i and ΔAy_i) at the excitation and emission wavelengths, respectively [14]; the acquisition of absorption spectra for the whole range of quencher concentrations followed an identical titration procedure.

2.2. Materials

Coffee grounds (CGs) from Nicola® premium blend were collected from automatic machines of Instituto Superior de Engenharia de Lisboa coffee shops. After collection, the CGs were dried in oven at 60 °C until constant weight, and refrigerated at 5 °C in polyethylene boxes until use.

Ethylenediamine (ED, >99.5%, Fluka, Sigma-Aldrich Corp., St. Louis, MO, USA), ortho-nitroaniline (o-NA; 98%, Acros Organics), meta-nitroaniline (m-NA; 99%, AcrosOrganics), para-nitroaniline (p-NA; 99%, BDH) and quinine hemisulphate monohydrate (QS, >98%, Fluka, Sigma-Aldrich Corp., St. Louis, MO, USA) were used as received. Urea was recristalized from ethanol. Ultrapure water (Milli-Q, Millipore; Merck KGaA, Darmstadt, Germany) was used in all experiments.

2.3. Synthesis of C-Dots from Coffee Grounds

C-dots were synthesized from CGs dispersed in water by a one-pot Mw-HTC procedure, using ethylenediamine or urea as additives, at 190 °C in a closed vessel for a certain selected time. After cooling to room temperature, the mixture was filtered through cellulose membrane (0.2 µm pore size), yielding brown solutions. Synthetic yields were calculated after rotary evaporation and drying of the solid residues. Water dispersions of C-dots in appropriate concentrations were used in the sensing assays.

3. Results and Discussion

3.1. Synthesis and Structural Characterization

The fluorescent C-dots here described were synthesized from CGs in an eco-friendly way. The effect of the residence time on the C-dots luminescence, keeping constant the reaction temperature (190 °C) and the amount of additive (0.16 massic ratio ED (or urea)/CGs) were evaluated (Table 1).

Under the tested conditions, the highest luminescent nanomaterials were obtained upon 3 h of irradiation (Table 1, entry 3).

The nature of the nitrogen-rich additive showed a relevant impact on the fluorescence quantum yield. Indeed, when the same conditions of those of entry 3 were applied to a mixture of CGs/urea (entry 5), a three-fold decrease of quantum yield was observed.

Analysis of characteristic functional groups at C-dots surface was performed by FTIR spectroscopy showing the most prominent bands at 3433 (O-H, str), 3260 (N-H, str), 2965, 2927, 2858 (C-H, str), 1666 (C=O, str), 1514 (N-H ben and C=C str), 1452 (CH_2, ben), 1382 (CH_3, ben) cm^{-1} (Figure 1).

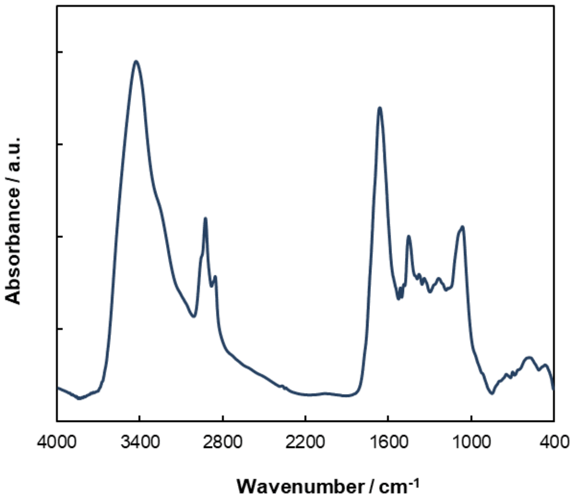


Figure 1. FTIR spectrum (KBr) of C-dots.

^{1}H NMR spectrum of the as-synthesized C-dots indicates the presence of aliphatic C-H resonances (0.7–2.8 ppm), a large set of peaks between 3.2 and 4.3 ppm assignable to CH-O and CH-N and aromatic protons from 6.6 to 8.5 ppm (Figure 2).

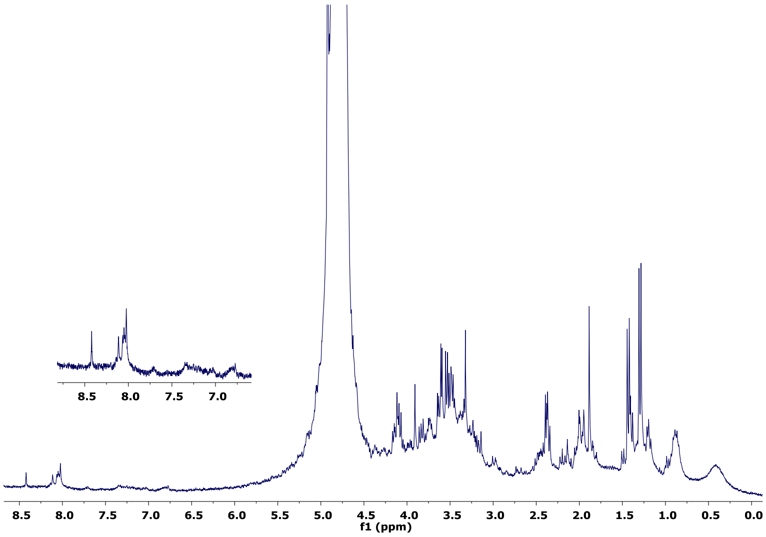


Figure 2. ^{1}H NMR spectrum of C-dots in D_2O.

3.2. Photophysical Properties

The photophysical properties of aqueous dispersions of C-dots were studied by UV-Vis and fluorescence spectroscopies. Ground-state absorption and steady-state fluorescence spectra are showed in Figure 3. The absorption spectrum exhibits bands peaking at ca. 285 nm and 325 nm, with a shoulder near 400 nm. The excitation spectrum shows that the main chromophores responsible for the emission appear at around 300, 348 and 392 nm. When excited at 380 nm, the emission spectrum revealed a band with maximum at 462 nm.

C-dots also display variable emission maxima, which are dependent on excitation wavelength (not shown).

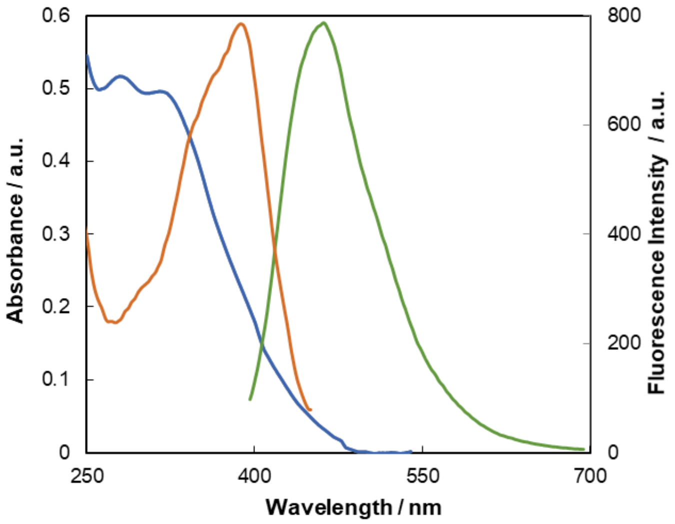
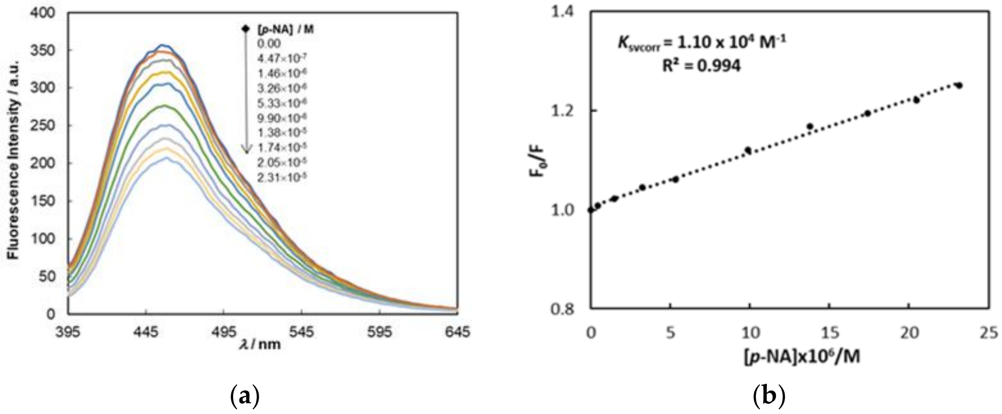


Figure 3. UV-Vis (blue line), excitation (orange; monitored at 462 nm) and emission (green line; λ_{exc} = 380 nm) spectra of aqueous dispersions (0.1 mg/mL) of C-dots.

3.3. Detection of Nitroanilines by C-dots

The potential application of C-dots as sensing materials for NAs was evaluated by fluorescence and absorption techniques. The experiments were performed with isomeric NAs in a concentration range of 4.47×10^{-7}–2.31×10^{-5} M, using C-dots aqueous dispersions of 0.01 mg/mL (Figure 4a; p-NA shown). 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 4b).



(**a**) (**b**)

Figure 4. (**a**) Emission spectra of C-dots (0.01 mg/mL) after successive additions (4.47×10^{-7}–2.31×10^{-5} M) of *p*-NA (λ_{exc} = 380 nm). (**b**) Stern-Volmer plot after correction for h-IFE.

It was found that C-dots shows high sensitivity for *p*-NA. Data for all NAs tested are shown in Table 2.

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	1.40×10^4 ($R^2 = 0.998$)	7.09×10^3 ($R^2 = 0.999$)
2	*meta*-NA	3.62×10^3 ($R^2 = 0.985$)	2.16×10^3 ($R^2 = 0.976$)
3	*para*-NA	3.10×10^4 ($R^2 = 0.999$)	1.10×10^4 ($R^2 = 0.992$)

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

4. Conclusions

This work showed that coffee grounds waste can be used as a suitable carbon source to produce fluorescent C-dots through sustainable one-pot Mw-HTC synthesis.

Several experimental conditions were investigated (residence time, temperature, and nature of additives) to modulate the photophysical properties. The highest luminescent carbon nanomaterials were evaluated as sensors for isomeric nitroanilines in aqueous solutions. A high selectivity and sensibility were attained.

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.

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