

Effect of Operating Parameters on the Properties of Carbon Dots from Spent Coffee Grounds

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ABSTRACT

Carbon dots (nanosized materials) exhibit excellent properties such as strong fluorescence, low cytotoxicity, biocompatibility, and good biodegradability which can be synthesized from various carbon sources such as biomass and food waste etc. Due to their unique properties, they are considered as potential alternatives to replace conventional metal-based quantum dots in a number of applications from energy storage, biomedicine to water treatment. In this work, we demonstrate an intensified and green approach to synthesize carbon dots from waste coffee. The synthesized carbon dots have application in sensing e.g. detecting heavy metals, contaminants in water, drug delivery and bioimaging.

KEYWORDS

Biomass;
Coffee Grounds;
Carbon Dots;
Hydrothermal Carbonisation;
Photoluminescence.

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1. Introduction

1.1. Carbon Quantum Dots

Since their discovery in 2004 (1), carbon dots (CDs) have attracted a lot of attention and are considered as a potential replacement for conventional semiconductor quantum dots in many applications such as bioimaging and sensing. (2) They are chemically inert, biocompatible and show insignificant cytotoxicity. They are easy to functionalize and very soluble in water. (3, 4) Carbon dots have great optical properties such as being highly fluorescent, non-blinking, resistant to photobleaching, (3, 4) broad excitation wavelength and a tuneable emission wavelength with changes to composition, size, shape, internal structure (3) and surface chemistry by modifying synthesis parameters. The mechanisms in which CDs show their photoluminescent properties is not yet fully understood. (5) The above properties make them great candidates for applications in live cell imaging, catalysis, electronics, biosensing, and targeted drug delivery. (6) Carbon dots can be synthesised cheaply through many different large-scale one step processes.

CDs can be produced via top-down or bottom-up approaches. Briefly, top-down methods take a large and define structured materials such as graphene oxides, (7) carbon nanotubes, (1) and carbon fibres (8) and reduce it down to nanoparticles. Bottom up methods make a nanoparticle from small building blocks such as citric acid or carbohydrates. (3, 9) the disadvantages of the top-down approach is that it uses expensive carbon sources, harsh reaction conditions, and longer reaction times. (10) Bottom-up strategies tend to have lower cost, more suitable for mass production and are more eco-friendly. (9)

Arc discharge is one of the top-down approaches of obtaining CDs (1) by passing a high current through a graphite rod acting as a cathode. The graphite is then evaporated by an electrical arc produced when a positive anode is placed a few millimetres away. A soot containing the products is deposited on the walls of the chamber. (11) Carbon dots can be obtained via purification and passivation of the products. (12)

Chemical ablation is a top-down process using strong acids e.g. sulphuric acid and nitric acid (13, 14) to carbonise small organic molecules to carbonaceous material via oxidation, which in turn can be

cut further into small sheets with more controlled oxidation reactions. This method can be large scale but suffers from drastic process and can use harsh conditions. (15)

The hydrothermal method is an eco-friendly bottom-up method using elevated temperatures (100°C–250°C) and high vapour pressure (16) in aqueous conditions to synthesise CDs cheaply and conveniently. The method is non-toxic, simple to operate, and does not require further passivation for photoluminescence (PL). However, the method does not account for impurities and has poor control over size. (17-20).

The template method is a bottom-up method that uses a mesoporous structure as a scaffold inside which the CDs are synthesised by calcination. The structure is then removed to obtain the dots. The advantage of this method is that size is highly controllable and uniform, but most dots require a second passivation step to show photoluminescence (21, 22).

Microwave synthesis is a bottom-up, quick, green, and economical process that uses a conventional microwave to assist in the carbonisation of carbon source to obtain carbon dots (23, 24). The advantage of this method is that the sample is heated directly which reduces heating time and exposure, which maximises yields. (25)

1.2. Coffee grounds

Coffee is consumed widely around the world and is one of the most traded crops in the world, around 10 million tonnes of coffee was consumed in 2020/21 (26). This leads to a significant spent coffee grounds that are currently landfilled (27). However, spent coffee grounds still contain many high value compounds such as oils, sugars, antioxidants and this could be exploited by the extraction of sugars or the production of biofuel. (28) or as a carbon source for carbon quantum dot synthesis. In 2012, Hsu et al. (29) were the first research team to develop carbon dots from coffee grounds which did not require strong acids or further passivation and modification. They produced CDs from spent coffee grounds via hydrothermal carbonisation at 300°C for 2 hours. They found in their research that CDs prepared from hydrophilic compounds have greater quantum yields and higher water solubility relative to hydrophobic ones. The dots have application in cell imaging and surface assisted laser desorption/ionisation – mass spectrometry.

Wang et al. (30) developed an eco-friendly and simple hydrothermal route to prepare fluorescent graphene CDs from coffee grounds which were then functionalized by polyethylenimine (PEI). The PEI-CDs were fluorescent and had a low cytotoxicity. These properties make them good candidates for application in bioimaging. The functionalised dots were highly sensitive to Fe^{3+} and Cu^{2+} ions, these ion-quenched PL characteristics, therefore these ions could be detected at a high sensitivity.

Crista et al. (31) compared the environmental impacts and the structural and luminescent properties of carbon dots synthesised from different carbon sources: biomass waste spent coffee grounds against standard precursors (citric acid and urea). The carbon dots from the standard precursors were characterised with an average size of 1.0–3.9 nm, a blue emission, and a quantum yield of 22.5%, compared to the spent coffee ground-based dots, characterised with a quantum yield of 2.9-5.8%. The dots can be used for sensing probes for Fe^{3+} in water. However, the spent coffee ground-based dots are more environmentally beneficial than carbon dots from standard precursors.

Xu et al. (32) used a microwave assisted hydrothermal approach to synthesise highly uniform carbon dots that had a height range of 1-3 nm with distinct photoluminescent emissions between 460 to 560nm from spent coffee grounds. The first step of the reaction was the microwave heating of coffee grounds with sulphuric acid to generate CD precursor. This precursor was then oxidised by nitric to yield the carbon dots to use in water purification.

In this research carbon dots were synthesised from spent coffee grounds using a two-step synthesis adapted Xu et al's (32) microwave method. The first step of the reaction was a hydrothermal synthesis of a carbon dot precursor from spent coffee grounds using a sulphuric acid catalyst. The precursor was then cut down to carbon dots using a nitric acid oxidation. Different catalysts, concentrations, and

holding time in the first hydrothermal step were investigated. The effect on the size and fluorescence of the resulting carbon dots will be demonstrated.

2. Experimental

2.1. Materials

Spent coffee grounds from a local café were used as the carbon source. sulphuric acid (95%, Sigma Aldrich) and tannic acid (powder, sigma Aldrich) were used as catalysts in the first step and nitric acid (70%, Sigma Aldrich) was used for the oxidation in the second step.

2.2. Characterisation

FT-IR was used for functional group analysis on the carbon dot precursors (Agilent Cary 630 FTIR Spectrometer) between 4000cm^{-1} and 650cm^{-1} with 16 scans at a resolution of 4cm^{-1} . Both the Carbon dot precursors and CD themselves were imaged using a transition electron microscope (Hitachi HT7800 120kV TEM) using a beam of 100kV. The samples were prepared by being dropped onto TEM grids and allowed to dry. UV-Vis was used to measure the absorption of the carbon dots (Jenway 730501 7305 UV Visible Spectrophotometer). The Photoluminescent properties of the dots were measured using an Edinburgh FLS980 photoluminescence spectrometer, equipped with a 450W Xenon arc lamp, Czerny Turner excitation and emission monochromators (1.8 nm/mm dispersion; 1800 grooves/mm) and a Hamamatsu R928 P photomultiplier tube (in a fan assisted TE cooled housing, operating temperature -20°C).

2.3. Carbon dot synthesis

This experiment was designed to investigate the effect of holding time and catalyst type and concentration on the resulting precursors and carbon dots. The holding time was varied between 2-4 hours, the catalysts tested were sulphuric acid in a concentration range of 0.005g/mL – 0.02g/mL and tannic acid at a concentration range of 0.005 – 0.05g/mL . A blank test without catalyst was also carried out. These reactions are outlined in (Table 1).

Tannic acid was chosen as the green catalyst because it is a biomolecule and is biocompatible and has been used in medicine for the treatment of burns. Its structure filled with OH groups was also a reason to break open the structure of cellulose in the spent coffee grounds in a similar manner to the sulphuric catalyst.

Table 1. Experimental conditions (holding time and catalyst concentrations) tested

<u>Sample code</u>	<u>Holding time (hours)</u>	<u>Concentration (g/mL)</u>
<u>Time Tests (TT)</u>		
TT-2H	2	0.01
TT-3H	3	0.01
TT-4H	4	0.01
<u>Sulphuric Acid Tests (SA)</u>		
SA-0.0	2	0.0
SA-0.005	2	0.005
SA-0.01	2	0.01
SA-0.02	2	0.02
<u>Tannic Acid Tests (TA)</u>		
TA-0.005	2	0.005
TA-0.01	2	0.01
TA-0.02	2	0.02
TA-0.05	2	0.05

A typical precursor synthesis was proceeded by mixing 0.5g of dried spent coffee grounds with 15ml of catalyst solution (Table 1) at a 1:30 ratio and placed into a 125ml volume PTFE sealed reactor. The reactor was then heated to 200°C for a fixed holding time (Table 1) in an oven. The mixture was then filtered using a $0.1\mu\text{m}$ filter paper to yield the solid carbon dot precursor which was dried at 60°C for 12 hours. FT-IR and TEM data were collected on the precursors.

The synthesis of the carbon dots from the precursors proceeded by mixing 50mg of each precursor with 15ml of 20% wt nitric acid and ultrasonicated at 60°C for 30 min. This mixture was then refluxed at 90°C for a further 30min. The resulting solution was then vacuum filtered using a 0.1µm vacuum filtration to yield a liquid that contains carbon dots. Rotary evaporation was used to yield a solution of carbon dots. TEM, UV-Vis, and PL data were collected on the carbon dot solutions. The full reaction pathway of both steps is outlined in Figure 1.

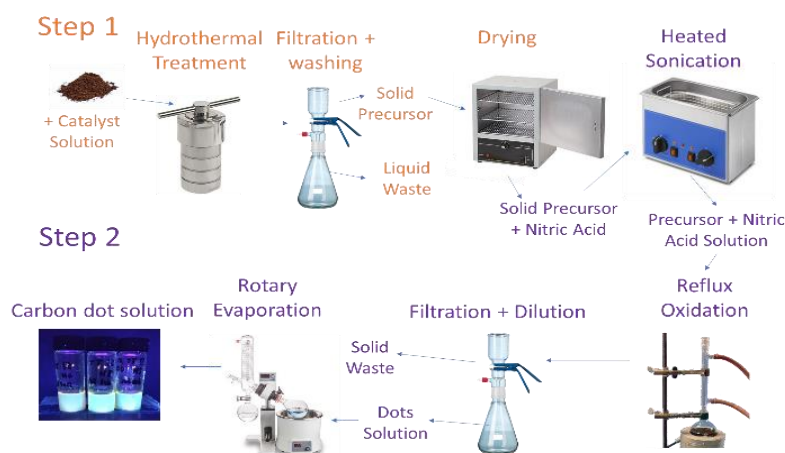


Fig. 1. Outline of the reaction pathway: the first step is coloured in orange and the second step coloured in purple

3. Results and Discussion

3.1. Precursor synthesis

3.1.1. FT-IR

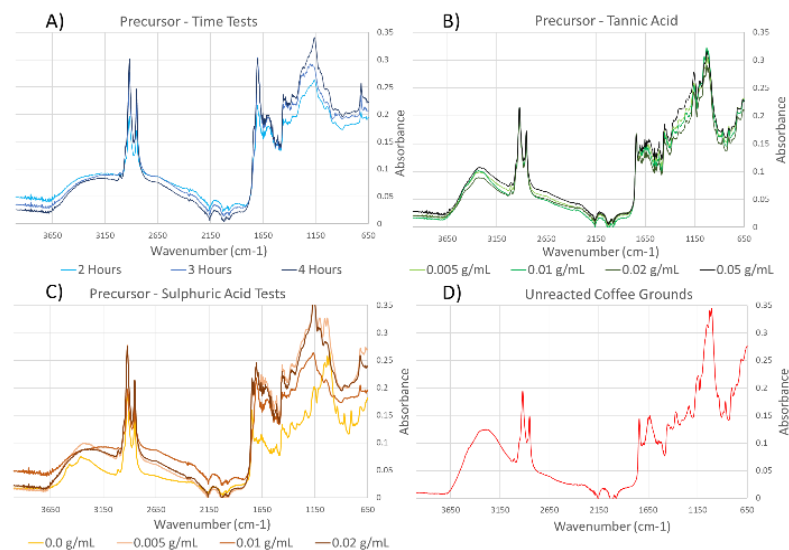


Fig. 2. FT-IR analysis of carbon dot precursors. A – holding time, B - Tannic acid tests, C - Sulphuric acid tests, D – Raw spent coffee grounds

Figure 2 presents the FT-IR data of precursors obtained at various holding time (Figure 2A), catalysts (Figure 2B: tannic acid; Figure 2C: sulphuric acid), and raw coffee grounds are also included for comparison (Figure 2 D). The time tests (Figure 2 A) show a double peak at ~2900 and 2850 cm^{-1} which corresponds to the C-H bond. The peak at 1700 cm^{-1} corresponds to the C-O bond, broad peak at ~1200 cm^{-1} corresponds to C=O. It is clear that the sulphuric acid catalyst introduces more oxygen containing groups into the precursor. It is also shown that increasing the retention time increases the intensity of the spectra which could indicates that increased retention time increases the amount of oxygen

containing groups on the surface of the precursor. Comparing the precursors with those produced by Xu et al. (32), it can be seen that the FT-IR was very similar.

The sulphuric acid series (Figure 2 C) of reactions FT-IR spectra shows the same peaks as the time tests apart from the test that had no acid as a catalyst where a FT-IR spectrum was similar to the raw spent coffee grounds. It was not clear the effect of the concentration of sulphuric acid on the precursor as there was no trend between the different concentrations. The intensity of the spectra for both the 0.005g/ml and 0.02g/ml reactions were similar and were more intense than the spectra for the original 0.01g/ml.

The FT-IR spectra of the precursors obtained tannic acid tests (Figure 2 B) were a lot closer to raw coffee grounds (Figure 2D) than the precursors synthesised with sulphuric acid. This is due to the wide alcohol peak at $\sim 3300\text{ cm}^{-1}$, the large peak at $\sim 1020\text{ cm}^{-1}$, strong carbonyl at $\sim 1740\text{ cm}^{-1}$, the fingerprint regions between 700 and 900 cm^{-1} . This is also the case for the precursor that used no catalyst.

From (Figure 2), it can be concluded that using tannic acid as a catalyst, or no catalyst, does not generate the same precursor as sulphuric acid over the tested conditions. A negligible difference between each spectrum of the tannic acid series so changing concentration of tannic acid had little effect on the FT-IR of the precursors.

3.1.2. TEM

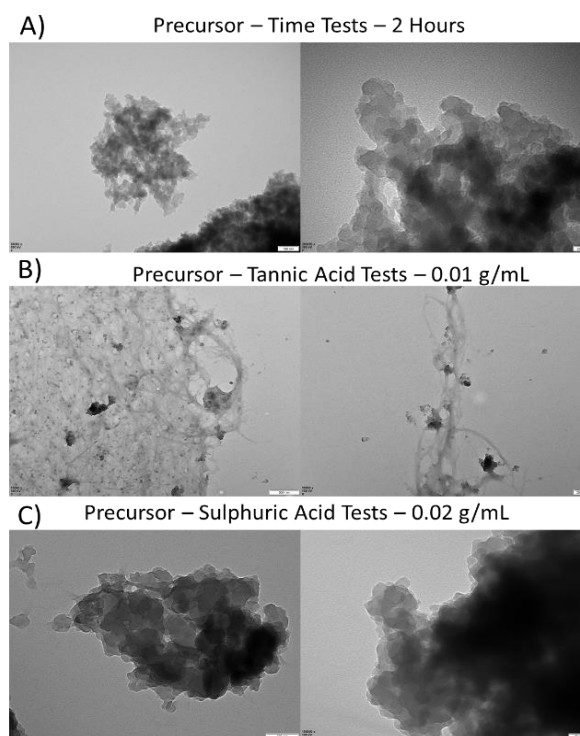


Fig. 3. TEM images of the precursor materials: A – 2 hour time test, B – 0.01 g/mL tannic acid tests, C – 0.02 g/mL sulphuric acid test

Figures 3 A and C show the graphitic layers of the precursor. These layered structures also resemble the structures seen in Xu et al. (32) TEM images. They described the structures as “*highly stacked sheets featuring tight interlaminar attractions and wide dimensional distribution*”. However, the precursor synthesised without a catalyst (0.0 g/mL) or with tannic acid show structures that are similar to Figure 3 B. which show a less ordered, more amorphous structure which include none of the features described above.

With this data and the FTIR data it can be deduced that using tannic acid or no catalyst does not produce the same precursor as the sulphuric acid tests.

3.2. Dot solutions

The dots that were synthesised using these precursors were also analysed using TEM, UV-Vis and photoluminescence spectroscopy

3.2.1. TEM

TEM was used to picture the dots, below is an example of these images from both the dots synthesised with no acid catalyst (Figure 4) and dots synthesised with a tannic acid catalyst (Figure 5)

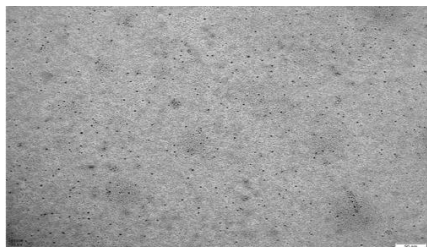


Fig. 1. TEM image of the dot solution from precursor synthesised with no catalyst 0.0g/mL

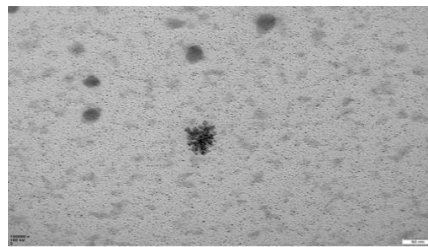


Fig. 2. TEM image of the dot solution synthesised from tannic acid precursor 0.02g/mL

It can be seen for these images that the dots are below 10 nm in diameter and are evenly distributed.

It is clear the general method in this study produces dots with or without catalyst. The dots from precursors that used sulphuric acid catalysts were larger (10-20nm). This indicates that not only is sulphuric acid catalyst not required to produce dots, but the dots also produced with a green/no catalyst are smaller size, which is more desirable for application in imaging.

3.2.2. Optical properties

UV-Vis

The UV-Vis was taken to investigate the absorbance of the carbon dot solutions and it was found that all the solutions had an absorbance between 280 and 300 nm, most of the values landing between 288 and 294 with no visible trend. It was shown that changing the catalyst, catalyst concentration and holding time had little effect on the absorbance wavelength (Table 2).

Photoluminescence

The photoluminescence tells a slightly different story. Initially the photoluminescence of the dot solutions was blue when excited by a UV lamp (Figure 6).

The solutions were then measured with a PL spectrometer at an excitation wavelength of 300nm. Figure 7 shows that changing the retention time, catalyst concentration and catalyst type had little difference in the emission wavelength of the photoluminescence its intensity. (Table 2 and Figure 7).

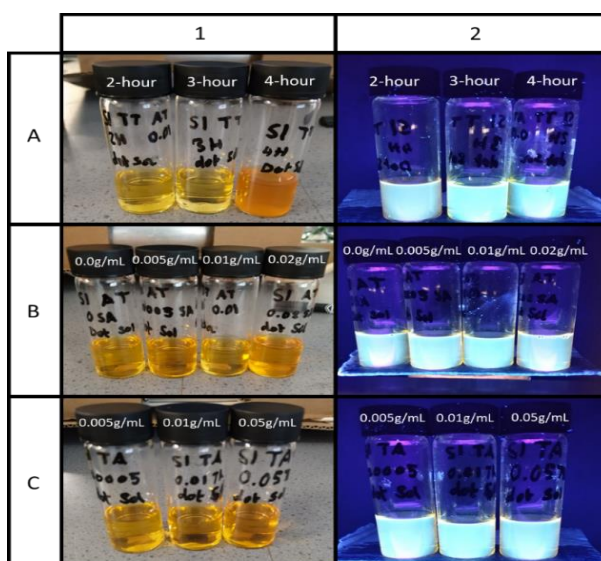


Fig. 6. Dot solutions under lab lights (1) and under UV-Light (2); A – dot solutions synthesised from time test precursors, B – dot solutions synthesised from sulphuric acid precursors, C – dot solutions synthesised from tannic acid precursors

Table 2. UV-Vis absorbance data and photoluminescence emission data of the dot solutions

Dot solution from precursor	UV-Vis		Photoluminescence	
	Absorbance	Wavelength	Intensity	Wavelength
TT 2H	0.054	290 nm	51700	430 nm
TT 3H	0.044	288 nm	45000	430 nm
TT 4H	0.051	292 nm	94800	417 nm
SA 0.0 g/mL	0.072	294 nm	34400	431 nm
SA 0.005 g/mL	0.099	292 nm	53200	432 nm
SA 0.01 g/mL	0.054	290 nm	51700	430 nm
SA 0.02 g/mL	0.054	288 nm	74300	436 nm
TA 0.005 g/mL	0.072	294 nm	68600	431 nm
TA 0.01 g/mL	0.100	288 nm	83200	430 nm
TA 0.02 g/mL	0.080	300 nm	19700	430 nm
TA 0.05 g/mL	0.103	288 nm	82100	433 nm

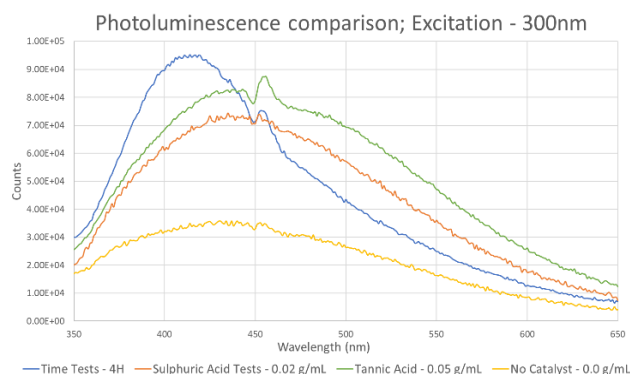


Figure 7. Photoluminescence data for the most intense carbon dot solution for each reaction set at an excitation wavelength of 300nm

The dot solution that produced the highest intensity were the dots produced from a precursor that had a retention time of 4 hours and a sulphuric acid catalyst in the precursor synthesis. It is clear that the longer retention time introduced some changes to the precursor that caused these dots to have a lower emission wavelength and more intense photoluminescence. Increasing the sulphuric acid catalyst concentration also increases the intensity of the photoluminescence of the resulting dots. These changes could be explained by the increase in abundance of surface groups of the precursors as shown in the intensity of the FT-IRs. These precursors go on to create dots that have lightly different surface chemistry, more analysis would be needed to confirm this. The dots that used tannic acid as their precursor show increase photoluminescence intensity when compared to sulphuric acid catalyst dots. They also show the same trend as increased intensity with increased concentration. This can also be explained by the surface chemistry they inherit from their precursors.

This data gives the conclusion that tannic acid is a better catalyst than sulphuric acid to synthesise the precursor since is it more green and safer to use and produces dots that are more luminescent and smaller. This data also shows that increased precursor retention time increases photoluminescence intensity and gives a more narrow and lower emission.

4. Summary and Conclusions

Carbon dots were synthesised by a two-step process, a hydrothermal carbonisation with an acid catalyst followed by an oxidation with nitric acid. This has been confirmed by the photoluminescence spectroscopy and TEM images. It has been seen that using different catalysts for the hydrothermal carbonisation changes the photoluminescence intensity of the dots. It was shown that tannic acid was

the superior catalyst as the photoluminescence of the dots is overall more intense than that obtained from the case using sulphuric acid or no catalyst and these dots are suitable for application as an imaging agent due to their small size and superior photoluminescence.

5. Future Work

Currently there is still more reaction series to be tested within this work and more data to be collected and analysed. The next reaction series will focus on the effect of the second step with holding time and nitric acid concentration, a greener alternative to the nitric acid such as ozone will also be tested. The solutions of the carbon dots will also be dialysed and freeze dried to obtain solid carbon dots. This will allow the yield to be calculated and XPS and FT-IR to be ran on the dots for surface analysis.

In the future the tannic acid will be used as the main catalyst in the hydrothermal treatments of the experiments going forward. More experiments will be completed on the pre-treatment of the spent coffee grounds and operating parameters for the hydrothermal treatment such as temperature and holding time whilst using the tannic acid catalyst.

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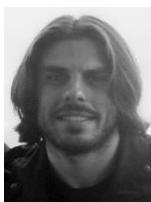
Thomas Wareing is a PhD student currently studying at Newcastle University, UK. He received his MSc in chemistry from the University of Central Lancashire, UK in 2018. His current post graduate work focuses on combining carbon dots and the layer-by-layer technique for a nanotheranostic treatment for cancer, his undergraduate dissertation focused on computational drug design for Alzheimer's disease. Since starting his PhD Thomas has published a review in *ACS Nano* entitled: Biomass-Based Carbon Dots: Current Development and Future Perspectives.



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Fabio Cucinotta received his academic trainings from University of Messina (BSc and Master, 2006), University of Münster (PhD, 2010) and University of Eastern Piedmont (post-doc fellowship, 2014), prior to his faculty appointment at Newcastle University, where is currently Lecturer in Physical Chemistry. His present research interests include molecular photophysics and supramolecular materials for light-harvesting and light-emitting devices.