

## BORON DOPED CARBON QUANTUM DOTS: PREPARATION, CHARACTERIZATION AND POTENTIAL APPLICATION

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### Abstract

When thinking about adding dopants to carbon quantum dots, the element boron, which has a similar atomic radius to carbon, is a rather natural candidate. However, the carbon quantum dots surface can drastically alter the electrical properties and, as a result, the optical behaviour of hetero-atoms with more electrons than carbon. Despite the fact that boron is a heteroatom with less electrons than carbon, the majority of research publications on boron addition that have been published focus on boron/nitrogen co-doping, and there is very little work that specifically discusses boron doping. The presented research illustrates a straightforward, environmentally friendly method for creating boron doped carbon quantum dots. This is the first report on boron doped carbon quantum dots microwave synthesis under specific reaction circumstances that we are aware of in the literature. Prepared boron doped carbon quantum dots showed high photo-catalytic activity towards the model organic dye Rose Bengal chosen for this purpose, with 84% of the Rose Bengal dye removed.

### Introduction

Carbon quantum dots (CQD) physical-chemical properties and ability to change them through doping by different hetero-atoms, gained research attention over the years [1], [2]. Nevertheless, finding the appropriate method for their preparation is a challenging task due to several issues such as high temperature, long hours and green medium for CQD synthesis. A variety of top-down and bottom-up techniques for CQD production have been developed over the years. The top-down method indicates the breaking of macro-molecules into small-sized CQD by physicochemical means, whereas the bottom-up method generally refers to the polymerization and carbonization of simple molecules into CQD through a chemical reaction. Because of its efficacy in synthesis and exploitation, the microwave (MW) pyrolysis process is one of the bottom-up methodologies that has attracted public attention [3]–[5]. This basic method of making CQD rich in oxygen-containing groups allows for quicker reactions, decreased energy usage, greater reaction yields, and increased particle size homogeneity while being environmentally friendly.

Despite the addition of both metal and non-metal (hetero-atom) dopants to the CQD matrix, the non-metal-based doping showed exceptional promise by enhancing their photo-luminescence powers. By substituting some carbon atoms with hetero-atoms like N, B, P, and S, one can modify the surface chemistry and electronic properties of CQD, which improves the structures' catalytic activity [6]. A wide range of possible uses for this material are made possible by the introduction of B dopant, which alters the surface chemistry and morphology of CQD. Carbon dots with boron doped could be used, among other things, for photo-catalytic destruction of

dangerous organics,  $\text{Fe}^{3+}$  detection, and radiometric intracellular pH monitoring in cancer cell lines [7]–[9].

Determination of the physical, chemical and optical properties is of great significance in finding the right and full range of the potential applications for the selected materials. Therefore, the presented paper focuses on the green synthesis of B-CQD using MW method and investigation on the morphological, elemental and optical properties with final application of prepared B-CQD in photo-catalytic reaction.

## Experimental

Two precursors were used in the B-CQD synthesis process. Boric acid ( $0.02 \text{ g ml}^{-1}$ ) and glucose water solution ( $0.1 \text{ g ml}^{-1}$ ) were mixed for 30 minutes at 600 rpm on a magnetic stirrer. The reaction mixture was then heated for 5 minutes at a fixed temperature ( $170 \text{ }^\circ\text{C}$ ) in a microwave reactor (Anton Paar Monowave 300), and then cooled to room temperature. The effective synthesis of B-CQD was demonstrated by the color change from translucent to light yellow that was seen. Dialysis ( $3.5 \text{ kDa}$ ) and filtration employing filters with various pore sizes were used to clean the sample.

Photocatalysis was carried out under constant conditions of reaction time of 300 minutes, medium pH of 7, B-CQD catalyst concentration of  $0.2 \text{ mg ml}^{-1}$ , and rose bengal (RB) dye as chosen pollutant in concentration of  $0.03 \text{ mM}$ . For the photocatalytic testing the home made photoreactor with six LEDs operating at  $370 \text{ nm}$  wavelength was used.

## Results and discussion

The elemental composition of the prepared B-CQD was investigated using XPS and FTIR analysis methods (Figure 1).

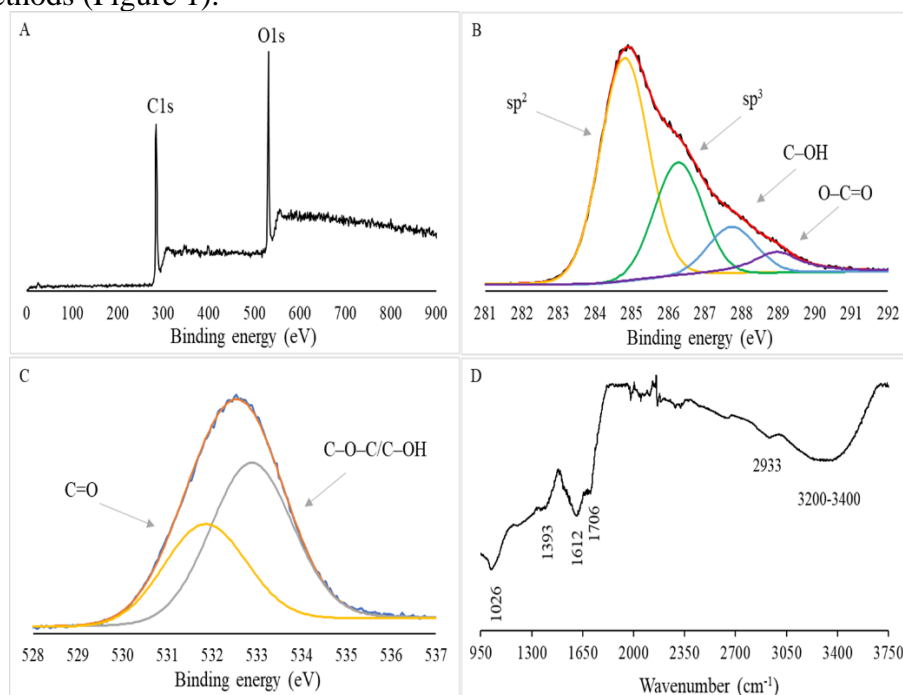


Figure 1. The B-CQD sample analysis showing the XPS full scan spectra (A), the C1s (B) and O1s (C), and FTIR (D).

From the obtained XPS results (Figure 1 A-C), the presence of carbon as  $\text{sp}^2$  and  $\text{sp}^3$ , and oxygen as C-OH and O-C=O, was confirmed after material preparation and purification. The presence of B dopant was not registered after XPS characterization due to the methods limit of detection which is below 0.3 at%. This was confirmed by performing additional

characterizations using ICP-OES analysis. The solid B-CQD nanomaterial contained  $0.506 \text{ mg g}^{-1}$  of B, which corresponds to a very low percentage of 0.051 B.

The FTIR study (Figure 1D) revealed peaks at  $3200\text{-}3400 \text{ cm}^{-1}$  and  $2933 \text{ cm}^{-1}$ , respectively, resulting from the stretching vibrations of the O-H and C-H groups. The B-CQD surface had a lot of hydroxyl groups, which have a favourable hydrophilicity. Peaks also appear at  $1706 \text{ cm}^{-1}$  and  $1612 \text{ cm}^{-1}$ , respectively, as a result of the stretching of the C=O and C=C bonds. The production of carboxylic acid groups on the surface of B-CQD nanoparticles was successfully demonstrated by the stretching of the hydroxyl and carboxyl groups as well as the symmetrical carbonyl stretching at  $1706 \text{ cm}^{-1}$ . The formation of unsaturated C=C bonds in the carbon cores was shown by the occurrence of the  $1612 \text{ cm}^{-1}$  signal. Signals were also found at  $1393 \text{ cm}^{-1}$  and  $1026 \text{ cm}^{-1}$ , which correlate to the stretching of B-O and B-C.

The investigation of the morphological features of synthesized B-CQD was obtained through AFM and TEM characterization (Figure 2). The AFM analysis (Figure 2A) showed monodispersing particles with a nearly spherical form with particle sizes ranging from 5 to 20 nm and average height between 1 and 5 nm. The obtained results were in correlation with TEM (Figure 2B) results were observed particles were between 7.5 nm and 17.5 nm in diameter.

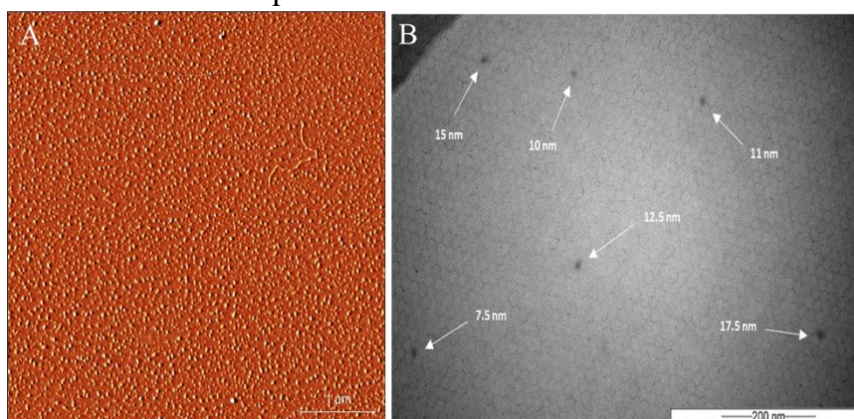


Figure 2. The B-CQD sample morphological analysis showing the AFM (A) and the TEM (B) images.

The optical properties of prepared B-CQD were examined by UV absorbance and PL (Figure 3). The absorbance at 268 and 356 nm, which corresponds to the existence of  $\pi\text{-}\pi^*$  transitions of aromatic  $\text{sp}^2$  domains (C=C) and  $n\text{-}\pi^*$  transitions of C=O bonds, was discovered by UV-vis spectroscopy (Figure 3A).

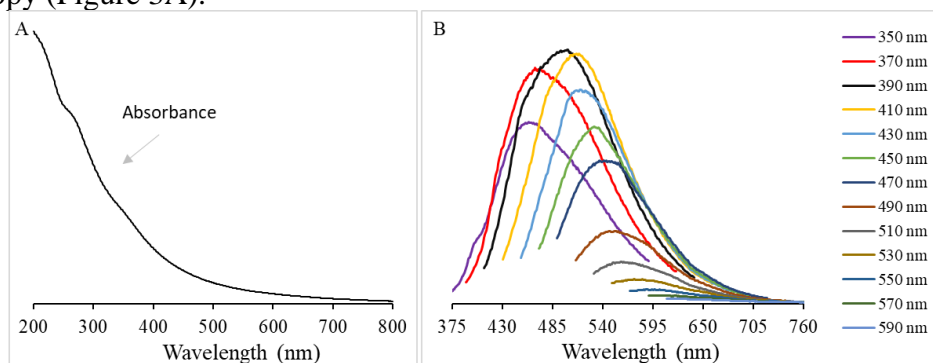


Figure 3. The B-CQD sample optical properties analysis showing the UV-vis absorbance (A) and the PL (B) spectrum.

The PL characteristics of carbon nanoparticles are caused by two different factors. Both intrinsic emission and emission from the defect state or trap state, which derives from various

surface functional groups connected to the carbon core, are related to particle size in one case. The emission of B-CQD in the 350-590 nm range displayed excitation dependence (Figure 3B). The maximum peak fluorescence emission was observed at 496 and 511 nm, respectively, after excitation at 390 and 410 nm, suggesting the blue-green emission spectrum. In this particular case, the Quantum Confinement Effect (QCE) model method is more likely to be the PL mechanism than emission from the defect state or trap state.

Prior to the photocatalytic activity investigation of B-CQD towards the RB organic dye degradation, the experiments of photolysis were performed in dark conditions and upon illumination (Figure 4). The obtained results suggested the RB dye self decomposition at 370 nm irradiation under 300 min of exposure up to 61%. However, in the presence of B-CQD nanomaterial, the adsorption in dark conditions was observed, where approximately 11% of the RB dye was adsorbed to the surface of the B-CQD photocatalyst. Under irradiation, the results obtained in the presence of a photocatalyst were comparable to the photolysis experiments in the first 90 minutes of irradiation. However, by prolongating the irradiation time up to 300 minutes, an obvious degradation effect and photoactivity of B-CQD nanomaterial was pronounced. The final result showed the high B-CQD nanomaterial potential in RB organic dye removal efficiency of 84% under 300 min of irradiation.

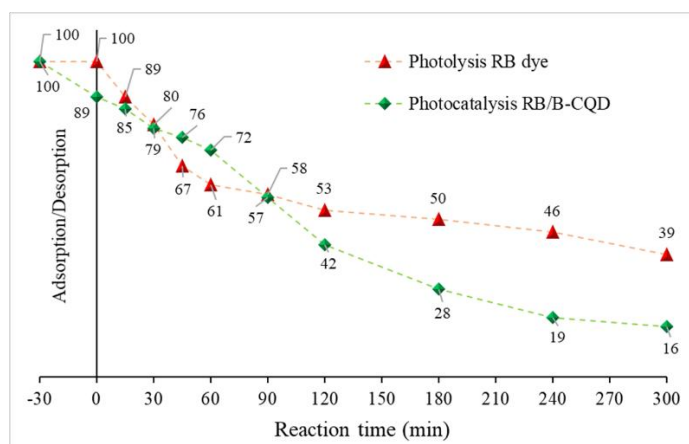


Figure 4. The B-CQD sample photocatalytic activity in the presence of RB organic dye.

## Conclusion

According to the study, it is possible to create boron-doped carbon quantum dots (B-CQD) using only glucose and boric acid and a microwave in under four minutes. The resulting B-CQD had an average diameter of 12 nm and were composed of negatively charged spheres. The hydroxyl, carbonyl, and carboxyl groups on B-CQD's surface are responsible for its excellent water dispersion capabilities. The rose Bengal (RB) dye was broken down by the B-CQD to 16%, respectively, within 300 minutes, demonstrating its excellent photocatalytic efficacy. The B-CQD produced in this work is shown to be an attractive option for the degradation of organic pollutants and ecological sustainability when considering its excellent photocatalytic activity and the ease with which it can be made using a microwave-assisted approach, without the need for time-consuming synthesis and purification.

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