

## SURFACE CHEMISTRY OF "BORON" DOPED CARBON QUANTUM DOTS

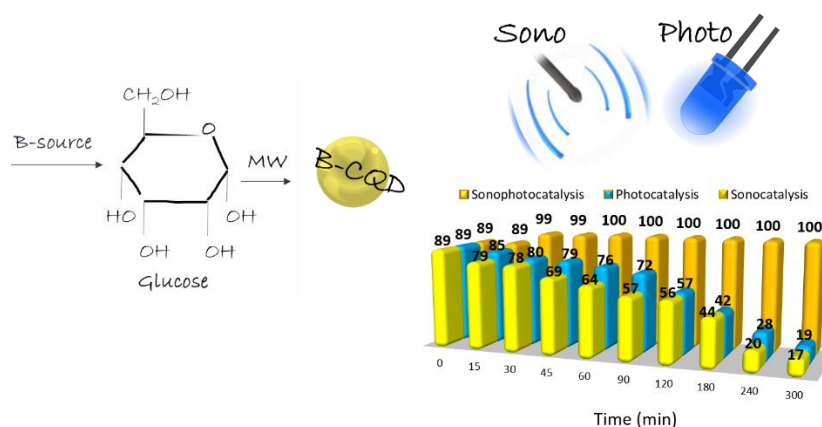
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### Abstract

Carbon quantum dots (CQDs), are a novel class of carbon nanomaterials that exhibit outstanding physical, chemical, and optical characteristics in addition to strong light absorption. By substituting some of the carbon atoms in CQDs for heteroatoms like N, B, P, and S, it is possible to modify the surface chemistry and electronic properties of the structures, boosting their catalytic activity. Adding B dopant to CQDs changes its surface chemistry and morphology, opening up a wide range of potential uses. The presented study illustrates a quick and environmentally friendly method for producing B-CQDs through microwave-assisted method. According to TEM characterization, the generated B-CQDs had a spherical form, an average diameter of 12 nm, and were negatively charged particles with good water dispersibility and no discernible aggregation. The thorough surface chemistry characterization revealed the presence of B-O and B-C bonds, as well as oxygen-containing surface functional groups in the form of hydroxyl, carbonyl, and carboxyl groups. Additionally, using an RB organic dye as a model molecule, the sonocatalytic, photocatalytic, and synergistic effects of the two processes were investigated.

### Introduction

A variety of top-down and bottom-up techniques for CQDs production have been developed over the years [1,2]. While the top-down method indicates the breaking of macromolecules into small-sized CQDs the bottom-up method generally refers to the polymerization and carbonization of simple molecules into CQDs. Because of effective microwave irradiation utilization, the microwave pyrolysis process is one of the bottom-up methodologies that has attracted widespread attention [3,4]. This simple method of producing CQDs rich in oxygen-containing groups allows for faster reactions, reduced energy usage, greater reaction yields, and increased particle size homogeneity while being environmentally friendly. When thinking about

adding dopants to CQDs, the choice of boron as carbon's next-door neighbor in the periodic table of elements with a comparable atomic radius (B: 0.080 nm; C: 0.077 nm) is rather obvious [5]. Adding B dopant to CQD changes its surface chemistry and shape, opening up a wide range of potential usage [6].

The usage of many hazardous organic compounds in the food, cosmetic, and textile industries increases rather fast on a daily level. Therefore, in order to protect the ecosystem, it is vital to treat these compounds since they are the main contributors to water pollution [7]. Due to their capacity to decompose some of the most tenacious water contaminants under the influence of ultrasonic cavitation and light irradiation, the photocatalysis, sonolysis, and sonophotocatalysis processes emerged as the most successful methods in water remediation [8–12].

Here we present a simple and cost effective bottom-up microwave approach for B-CQDs synthesis from glucose as carbon precursor. After detailed characterization of the B-CQDs physical-chemical properties the photo activity of the dots was examined on a model molecule of Rose Bengal organic dye. The synergistic effect of both sono and photo reaction conditions was confirmed after 300 min of system exposure.

### Experimental

The glucose water solution ( $0.1 \text{ g ml}^{-1}$ ) and boric acid ( $0.02 \text{ g ml}^{-1}$ ) were stirred for 30 min on a magnetic stirrer at 600 rpm, followed by heating in a microwave reactor (Anton Paar Monowave 300) for 5 minutes at a fixed temperature ( $170 \text{ }^\circ\text{C}$ ), to prepare B-CQDs.

Under constant settings of medium pH 7, reaction time 300 min, B-CQD catalyst concentration ( $0.2 \text{ mg ml}^{-1}$ ), and RB dye concentration ( $0.03 \text{ mM}$ ), tests on sono-, photo-, and sonophotocatalysis were conducted. For the sono testing the tip sonicator with set pulse was applied, while for the photo testing the photoreactor made in our group with six LEDs (6W, 370 nm) was used.

### Results and discussion

Exploring the morphology of obtained B-CQDs using TEM, the dots with average particle size diameter between 7.5 to 17.5 nm were observed (Figure 1A). Such a small sized particles showed a good water dispersability without any tendency towards aggregation/agglomeration (Figure 1B). Using UV-vis and PL spectroscopy, the optical characteristics of the B-CQD were investigated (Figure 1C, D). The absorbance at 268 and 356 nm, which corresponds to the existence of  $\pi\text{-}\pi^*$  transitions of aromatic  $\text{sp}^2$  domains ( $\text{C}=\text{C}$ ) and  $\text{n-}\pi^*$  transitions of  $\text{C}=\text{O}$  bonds, were detected by UV-vis spectroscopy (Figure C). The PL characteristics of carbon nanoparticles are usually triggered by two factors; one is related to the particle size while the second one is connected to the emission from the defect state or trap state caused by various surface functional groups connected to the carbon core. In the 350-590 nm range, the emission of B-CQDs showed evidence of excitation dependence (Figure 1D). The maximum peak fluorescence emission was observed at 496 nm, after excitation at 390, suggesting the blue-green emission spectrum.

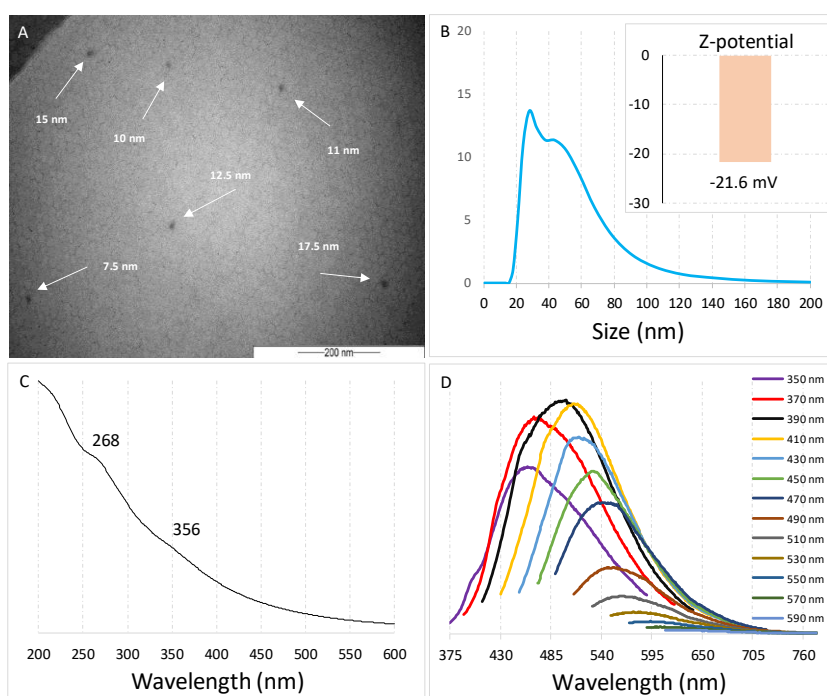


Figure 1. TEM morphology (A), DLS with Z potential measurements (B) and Absorbance/emission spectra (C) for B-CQDs.

According to the FTIR spectroscopy (Figure 2A), examination of the B-CQDs sample indicated the presence of signals at 3200-3400, 2933, 1706, 1612  $\text{cm}^{-1}$  attributed to the O-H and C-H groups, and C=O and C=C bonds, respectively. Additional signals at 1393  $\text{cm}^{-1}$  and 1026  $\text{cm}^{-1}$  correspond to B-O and B-C stretching vibrations.

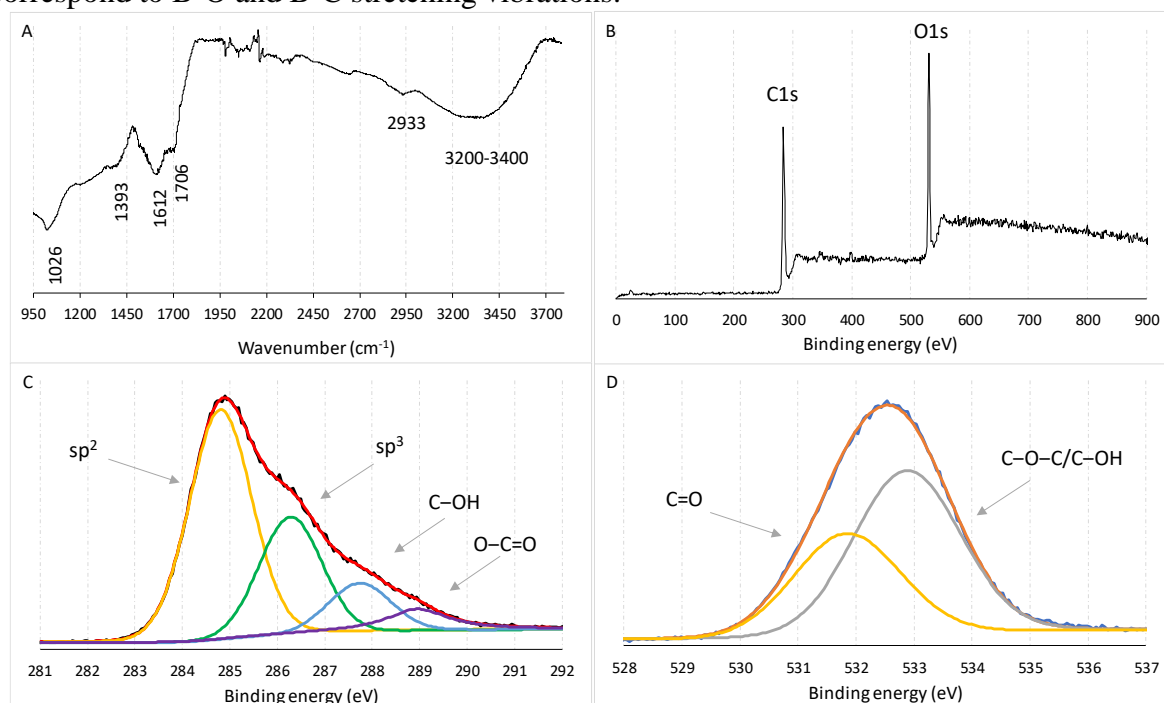


Figure 2. The FTIR results (A), the full scan XPS spectra (B), and the deconvolution of C1s (C) and O1s (D) for the B-CQDs.

Nevertheless, the full scan spectra did not show any existence of B dopant (Figure 2B). Therefore, an additional characterization, using ICP analysis, was performed confirming the presence of B dopant but in a small percentage. The B dopant was present as 0.506 mg per gram of B-CQDs, which was below the detection limit of XPS analysis (0.3 at%).

Under constant conditions of the dye and catalyst concentrations, medium pH, reaction temperature, and time, the synergy of the sono and photo effect on the RB dye removal efficiency was investigated. By keeping the reaction mixture under dark conditions, 11% of the RB dye was adsorbed on the catalyst surface. Introduction of the sono effect led to desorption of the dye due to the strong pulse of the ultrasound tip. On the contrary, the photo treatment resulted in a dye degradation up to 81% after 300 min of irradiation in the presence of B-CQDs as photocatalyst (Figure 3A).

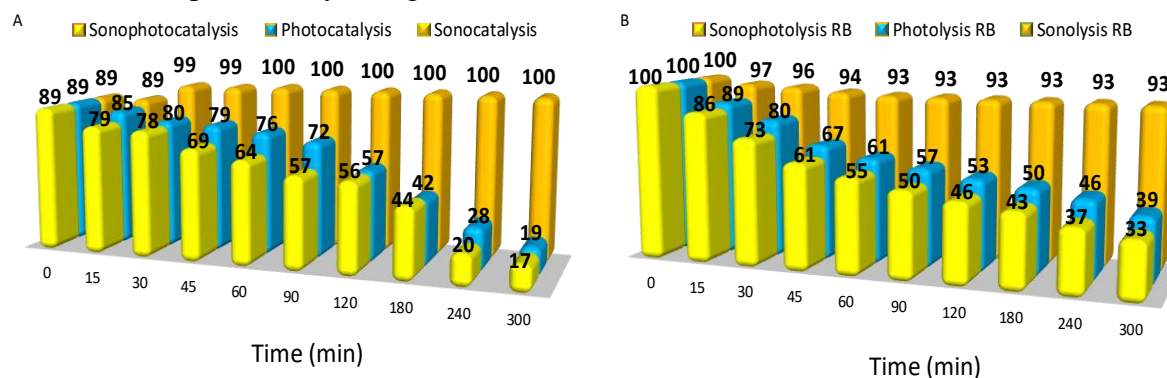


Figure 3. The results of sono, photo and sono-photo experiments: in the presence of a B-CQD catalyst (A) and control experiments without a catalyst (B).

The synergy of the sono-photo effect gave even better results with 17% of residual RB dye after 300 min of treatment (Figure 3A). When comparing obtained results with degradation efficiency in the absence of a B-CQD catalyst (Figure 3B), a much lower degradation percentage was observed in the same time frame. The final result suggested residual RB dye percentage of 93, 39, and 33 under sono, photo and sono-photo effect, respectively.

## Conclusion

Presented work shows a simple and fast microwave assisted synthesis of B-CQDs under mild reaction conditions such as 170 °C and 5 min, from glucose water solution and boric acid. Produced B-CQDs with as small percentage of introduced B dopant were spherically shaped dots with average diameter of 12 nm and strong light absorption capacity. Investigating the sono, photo and sono-photo synergy on a RB dye removal efficiency, the B-CQDs acted as a catalyst, improving the degradation percentage after 300 min of the exposure when compared to the control experiments. In comparison to a separate sono and photo method, the results showed that the sonophotocatalytic process had a high synergy index (>1).

## Acknowledgements

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