MICROWAVE-ASSISTED SYNTHESIS OF N-DOPED CARBON QUANTUM DOTS FOR THE PHOTOCATALYTIC REMOVAL OF METHYLENE BLUE FROM WASTEWATER

Dejan Kepić[1], Jovana Prekodravac[1], Bojana Vasiljević[1], Dragana Jovanović[1], Duška Kleut[1], and Biljana Todorović Marković[1]

[1] *Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, P.O.B. 522, 11001 Belgrade, Serbia*
e-mail: d.kepic@vin.bg.ac.rs

Abstract
Wastewater treatment is an emerging problem in the industrialized world. The development of new semiconducting materials with the potential to be used in photocatalysis is the focus of the scientific community. Here, we present the synthesis of N-doped carbon quantum dots (N-CQDs) using microwave radiation. N-CQDs were synthesized by irradiation of glucose solution in the presence of ammonia hydroxide as a nitrogen doping agent at low temperature (100 °C), low applied microwave power (100 and 200 W), and for a short period of time (60 s). The possible application of N-CQDs as a catalyst for photocatalytic degradation of Methylene Blue (MB) dye under blue light, green light, red light, and daylight was investigated. The highest values of MB degradation were observed for the samples exposed to red light with a maximum of 58.8 % for N-CQDs sample prepared at the reactor power of 200 W exposed to red light for 2 h.

Introduction
With the rapid industrial development and production of goods, industrial effluents became a big problem for the environment. The release of toxic chemicals in water, soil, and air constantly increases in the past decades, which consequently increases the need for the special treatment of waste material. Various organic dyes commonly used in the industry show mutagen and cytotoxic behavior [1]. Among different methods for the removal of dyes from wastewater, photochemistry has big potential to solve this problem. The size of the bandgap of semiconducting catalysts dictates the wavelength of the absorbed light. Recently, scientists put an effort to find semiconducting material with smaller bandgaps to improve visible light absorption. Besides, to exploit the ability of reactive oxygen species (ROS) to breakdown the dye molecules, it is important to find a catalyst with bandgap close to the redox potential of $H_2O/\cdot OH$ couple. To date, many heterogeneous catalysts are reported for the removal of dyes from wastewater [2-4].
The emerging interest in carbon nanomaterials brought to the scene new materials for the application in photocatalysis [5]. A new zero-dimensional carbon-based nanomaterial, carbon quantum dots (CQDs), recently draw attention due to their extraordinary properties. They are water dispersible, non-toxic, biocompatible, and economically and environmentally friendly, and they possess semiconducting character with a tunable energy bandgap that can be directed by the introduction of selected functional groups or heteroatom into their structure [6,7]. Nitrogen proved to be an effective heteroatom for doping of various carbon nanomaterials since it greatly influences the electronic properties of the material [8-10]. Although many methods for the N-doping of CQDs are reported so far, the majority of them are complex, time-consuming, and expensive. On the other hand, microwave-assisted synthesis accelerates chemical reactions at low temperatures and therefore can be applied for fast and efficient synthesis of N-doped CQDs (N-CQDs).

In this paper, a fast preparation of N-CQDs using microwave irradiation is demonstrated. The synthesis of N-CQDs from glucose solution in the presence of ammonia hydroxide as a nitrogen doping agent was conducted under microwaves with reactor power of 100 and 200 W for 60 s. The possible application of N-CQDs as a catalyst for photocatalytic degradation of Methylene Blue (MB) dye under blue light, green light, red light, and daylight was investigated.

Experimental

For the N-doped CQDs synthesis, 10 wt.% glucose solution in water was mixed with 25 % ammonia hydroxide in ratio 5:1. The reaction mixture was heated in microwave reactor (CEM Discover BenchMate) for 1 minute at a fixed temperature of 100 °C and microwave power of 100 and 200 W. Further in the text the samples are labeled according to the reactor power N-CQDs-100 and N-CQDs-200, respectively. After cooling to room temperature at atmospheric conditions, the samples were dialyzed (300 Da) for 5 days and filtered (membrane pore sizes between 450 and 10 nm). The morphology analysis was performed using TEM JEOL Jem 1210 Electron Microscope operating at 120 kV. For the analysis, the N-CQDs samples were prepared by drop-casting of the samples onto carbon-coated TEM copper grid 200 mesh. ATR FTIR spectra were obtained at Nicolet 8700 spectrometer with spectral resolution of 4 cm^{-1}. The UV-Vis absorption spectra were measured using Avantes UV-Vis spectrophotometer (Apeldoorn, The Netherlands). N-CQDs water solutions with concentration of 1 mg/ml were mixed with MB (0.03 mM) and exposed to blue light (λ=470 nm), green light (λ=530 nm), red light (λ=630 nm), and daylight (solar light on a window ledge without light flux concentration, May 30th, 2018) for 2 and 3 h. UV-Vis measurements were performed immediately after the exposure of the selected time period.

Results and discussion

Water solution of glucose and ammonia hydroxide was irradiated in microwave reactor at two different reactor powers of 100 and 200 W. The formation of N-CQDs formation is indicated by the change of the color of the reaction mixture to light brown for N-CQDs-100, and dark brown for N-CQDs-200. The morphology of the samples was characterized by TEM microscopy and the representative TEM images for samples synthesized at 100 and 200 W are presented in Figure 1 a) and b).

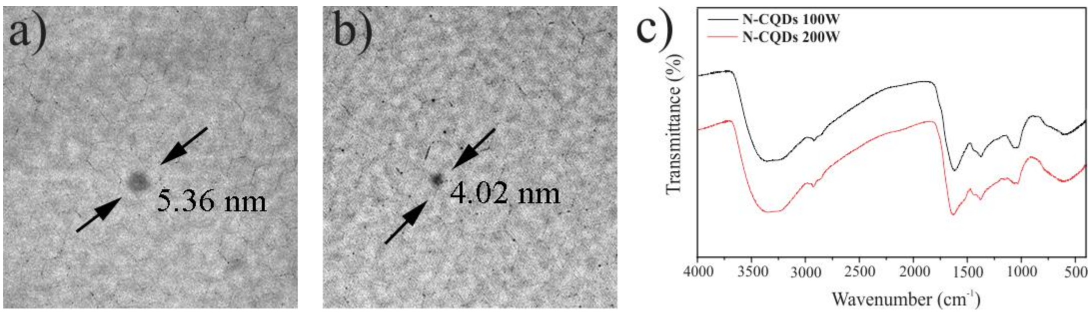

Figure 1. TEM images of N-CQDs samples synthesized at a reactor power of a) 100 W and b) 200 W, and c) FTIR spectra of N-CQDs samples.

The prepared N-CQDs have spherical shapes for both the applied reactor power. According to the microscopy analysis, the majority of particles have diameters of up to 30 nm. The FTIR spectra of N-CQDs synthesized at 100 and 200 W (Figure 1c) show a broad peak at 3400 cm^{-1} that originates from the stretching vibrations of O-H from carboxylic groups. The peak of N-H stretching vibrations from amine group at 3300 cm^{-1} is also present. Among these, peaks that correspond to C-H vibrations at 2929 and 2861 cm^{-1}, C=C vibrations at 1625 cm^{-1}, C-N bonds from amide groups at 1385 cm^{-1}, and C-O stretching vibrations at 1044 cm^{-1} are also present [11,12]. The presence of polar oxygen-related functional groups in the N-CQDs structure is responsible for their good water dispersibility.

Photocatalytic degradation of MB in the presence of synthesized N-CQDs was evaluated under a broad spectrum of wavelength, including blue light, green light, red light, and daylight. UV-Vis spectra of MB/N-CQDs exposed to these wavelengths are shown in Figure 2.

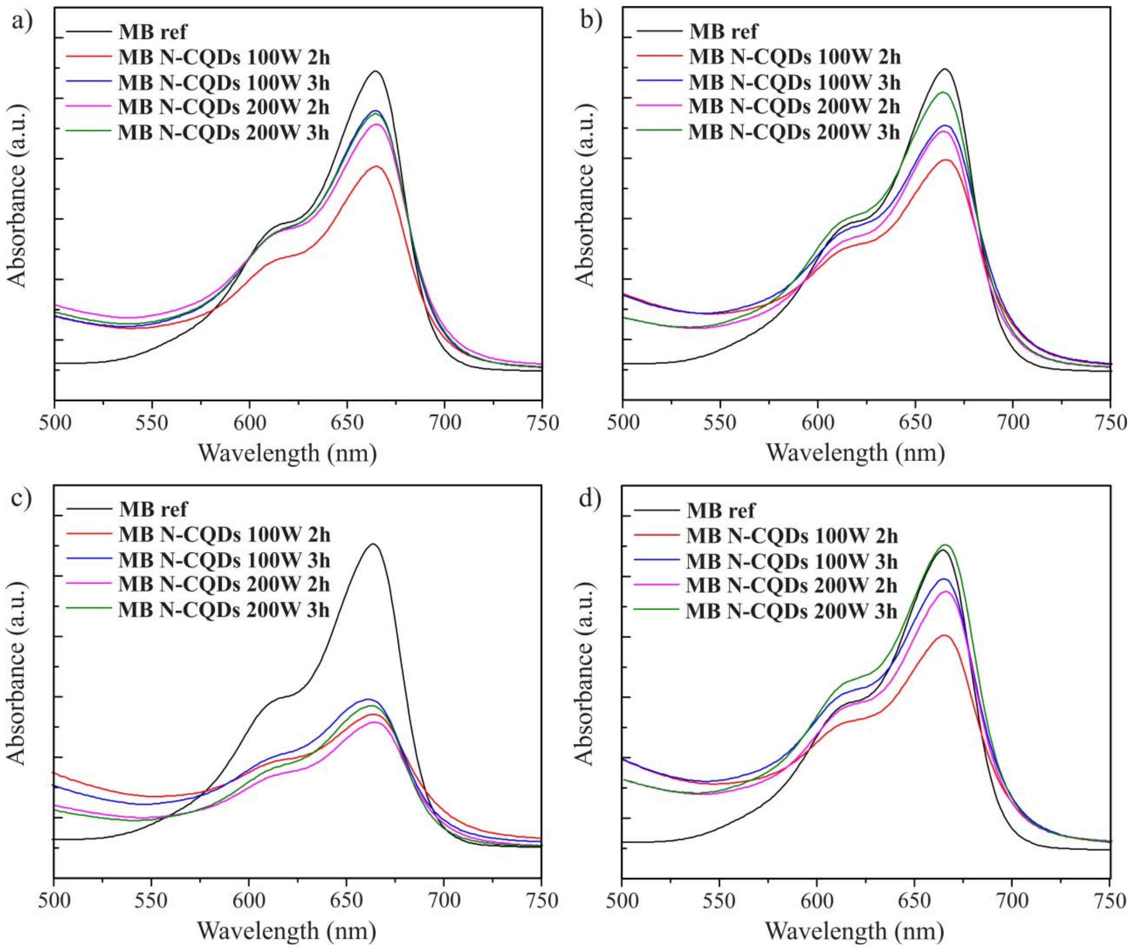

Figure 2. UV-Vis spectra of MB/N-CQDs exposed to a) blue light, b) green light, c) red light, and d) daylight for 2 and 3 h.

Since the concentration of MB is proportional to the absorbance of MB according to Beer-Lambert law, the degradation efficiency of MB can be calculated from the formula:

$$R = (C_0-C)/C_0 \times 100\ \% = (A_0-A)/A_0 \times 100\ \%$$

where A_0 and A are the absorbances, and C_0 and C are concentrations of MB in time 0 and t. For the constant amount of MB (0.03 mM), we examined the effect of the exposure time to the degradation of MB. Samples were exposed for 2 and 3 h to the blue light, green light, red light, and daylight. The results are presented in Table 1. As it can be seen, the highest values of MB degradation is observed for red light exposure, reaching values of 56.1 % and 51.5 % for MB/N-CQDs-100, and 58.8 % and 53.1 % for MB/N-CQDs-200. On the other hand, the lowest values of MB degradation is observed for MB/N-CQDs-200 exposed to green light and daylight for 3 h.

Table 1. Calculated degradation efficiency (in %) of MB in the presence of N-CQDs.

	Blue light λ=470 nm	Green light λ=530 nm	Red light λ=630 nm	Daylight
MB/N-CQDs-100 2 h	32.5	30.1	56.1	29.2
MB/N-CQDs-100 3 h	13.9	19.2	51.5	10.5
MB/N-CQDs-200 2 h	18.8	20.8	58.8	15.8
MB/N-CQDs-200 3 h	15.5	7.5	53.1	2.0

Conclusion

In this paper, a fast and efficient method to synthesize N-doped CQDs employing microwaves at two different reactor power of 100 and 200 W is described. N-CQDs were prepared from glucose solution in ammonia hydroxide as a nitrogen doping agent for 60 s of irradiation at 100 °C. Obtained N-CQDs have spherical morphology of up to 30 nm in diameter. The presence of oxygen-related functional groups in the structure makes N-CQDs water dispersible. Photocatalytic degradation of MB was evaluated under the exposure of samples to blue light, green light, red light, and daylight, and degradation efficiency was calculated. It was found that the highest degradation efficiency show samples exposed to red light, with the highest value of 58.8 % for MB/N-CQDs-200 sample exposed for 2 h.

Acknowledgements

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