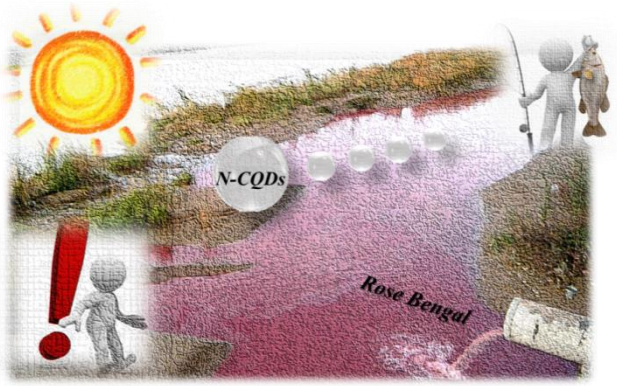
MICROWAVE SYNTHESIS OF N–CQDs: EFFECT OF WAVELENGTH ON DEGRADATION OF ORGANIC POLLUTION IN WATER

Jovana Prekodravac[1], Bojana Vasiljević[1], Dragana Jovanović[1], Dejan Kepić[1], Svetlana Jovanović Vučetić[1], Milica Budimir[1] and Biljana Todorović Marković[1]

[1]*Vinča Institute of Nuclear Sciences – National Institute of Republic of Serbia, University of Belgrade, Belgrade, Serbia*
e-mail: prekodravac@vin.bg.ac.rs

Abstract
Industries today realis high amounts of different hazards into the environment without any pre–treatment, which is why the remediation from organic pollution still represents one of the most important issues in waste water treatment. Organic dyes from textile industry are one of the extremely geno–toxic and cyto–toxic pollutants. Thus, finding the appropriate photocatalyst for the treatment of contaminated water under sunlight is still a challenging work from economical and green chemistry approach. Here we present a microwave assisted synthesis of nitrogen doped carbon quantum dots with high efficiency in degradation of Rose Bengal organic dye from water under visible, blue, green and red light irradiation in batch system. The effect of microwave irradiation power and time on size and photocatalytic activity of synthesized dots were also investigated.



Introduction
Organic dyes, as waste materials released daily into the environment without special treatment from the textile industry, are causing significant environmental issues [1]. Dyes such as Rose Bengal (RB), Methylene Blue (MB), Congo Red (CR) and Methyl Orange (MO) are extremely gene–toxic, mutagenic and cytotoxic organic dyes [2–4]. Therefore, the researchers are focused on developing different methods for overcoming these difficulties. Semiconductor heterogeneous photocatalysis proved to be an encouraging method for the degradation of industrial dyes. However, photocatalysis still requires research efforts in finding new semiconducting materials with smaller bandgaps for enhancing visible light absorption [5]. Carbon quantum dots (CQDs) come from carbon based nanomaterial family with significant attention from economic and environmental aspects. CQDs are water dispersible materials, due to a large number of oxygens–related groups (carbonyl, carboxyl and hydroxyl) whose properties could be significantly influenced through chemical modification [6–10]. Most of synthetic methods for synthesis and doping of CQDs are complex, economically affordable or time consuming [11, 12], quite the reverse, microwave (MW) assisted method can accelerate chemical reactions at milder reaction conditions. Here we report MW assisted synthesis of N–

CQDs with potential application in water treatment for removal of toxic organic dye RB through exposure to the visible light as well as the blue, green and red light illumination.

Experimental

The MW synthesis of N–CQDs was performed as we described in our previous work [13]. The 10 wt% of glucose water solution containing ammonia hydroxide as a nitrogen doping agent were heated in microwave reactor for 1 min, at fixed temperature (100 °C) and with applied microwave power of 100W and 200 W. The color of the MW treated solutions changed from transparent brown as a result of the N–CQDs formation. The samples were dialyzed (300 Da) for several days and filtrated through filters with different pore sizes. The synthesized N–CQDs were dispersed in RB water solution and exposed to visible light irradiation from window ledge as well as to blue, green and red light illumination using lamp (3W).

Results and discussion

The morphology of synthesized N–CQDs was examined by AFM microscopy. The top view AFM images of synthesized samples presented in Figure 1 a, c, show that N–CQDs have spherical like shapes. Measurements of particles thickness showed 1.2 nm for 100W samples and 0.9 nm for 200W samples indicating the single layer dots formation [13]. The real particle diameters of the particles measured by AFM, over more than 100 dots for each sample were in the range from 7 to 30 nm. Thus, increasing the MW power during synthesis resulted in formation of 90% N–CQDs with diameter lower than 18 nm.

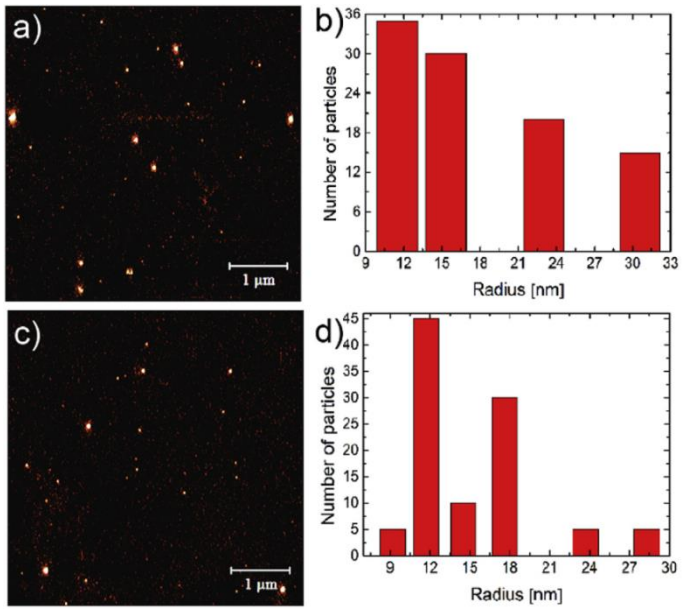


Figure 1. AFM analysis of synthesized N–CQDs samples: top view AFM image and real particle distribution for samples synthesized under 100W (a, b) and 200W (c, d).

The XPS results resolved that increase of applied MW power induces the increase of C sp^3 comparing to the sp^2 domains (Table 1), suggesting that synthesized dots are carbon nanodots consisting of sp^3 carbon matrix with sp^2 domains. The increase of applied MW power induced the decrease of pyrrolic–N and graphitic–N bonds while there is an increase of pyridinic/NH_2 bonds. The content of oxygen functional groups decreases, which could indicate the lowering of surface defects in the samples.

Table 1. The detail XPS analysis of the samples synthesized at 100W and 200W.

	Sample at 100W		**Sample at 200W**	
Name	***Peak BE (eV)***	***Atomic %***	***Peak BE (eV)***	***Atomic %***
C1s	285.8	66.4	285.5	69.2
O1s	532.2	23.5	532.1	19.1
N1s	400.0	10.1	399.9	11.8
C1s sp^2	284.5	18.9	284.5	18.8
C1s sp^3	285.1	22.7	285.1	28.2
C1s C–O	286.1	43.0	286.0	37.5
C1s C=O	286.9	5.6	286.9	5.0
C1s O–C=O	288.8	3.2	289.2	0.6
C1s NC=O	287.9	6.6	287,9	10.0
N1s pyrrolic	400.4	23.4	400.4	20.8
N1s pyridinic/NH_2	399.4	64.6	399.4	69.3
N1s graphitic/NH_3^+	401.7	12.0	401.6	9.8

The photocatalytic activity of synthesized materials was examined for photocatalytic degradation of one of the most dominant dye in textile industry (RB). The photocatalytic degradation efficiency of RB by N–CQDs material was monitored through decrease in the absorption peak intensity designated at 549 nm with a shoulder at 520 nm, both characteristic for pure RB dye. In our previous work we presented the decomposition of RB in the presence of N–CQDs under visible light irradiation explaining the effect of medium pH, contact time and catalyst concentration. Therefore here we have decided to explore how irradiation under different wavelengths affects the decomposition rate after 2h of irradiation. After performing reactions under the same reaction conditions such as using catalyst in concentration of 1 mg/ml, adjusting reaction medium to pH 7 and by exposing samples to the visible light (380–780 nm) or its components: blue light (380–500 nm), green light (500–570 nm) and red light (625–740 nm), different results were confirmed (Figure 2.). Exposure to the wavelengths shorter (Figure 2a) than absorption wavelength of pure RB resulted in the lowest values of degradation percentages, comparing to the green and red light experiments (Table 2). Similar observations were made comparing results after irradiation at longer wavelengths above 600 nm, and irradiation under wavelength region for RB absorption between 500 and 570 nm. However, the highest degradation percentage was observed after performing experiments under visible light irradiation where over 94% of RB dye was successfully decomposed (Figure 2d).

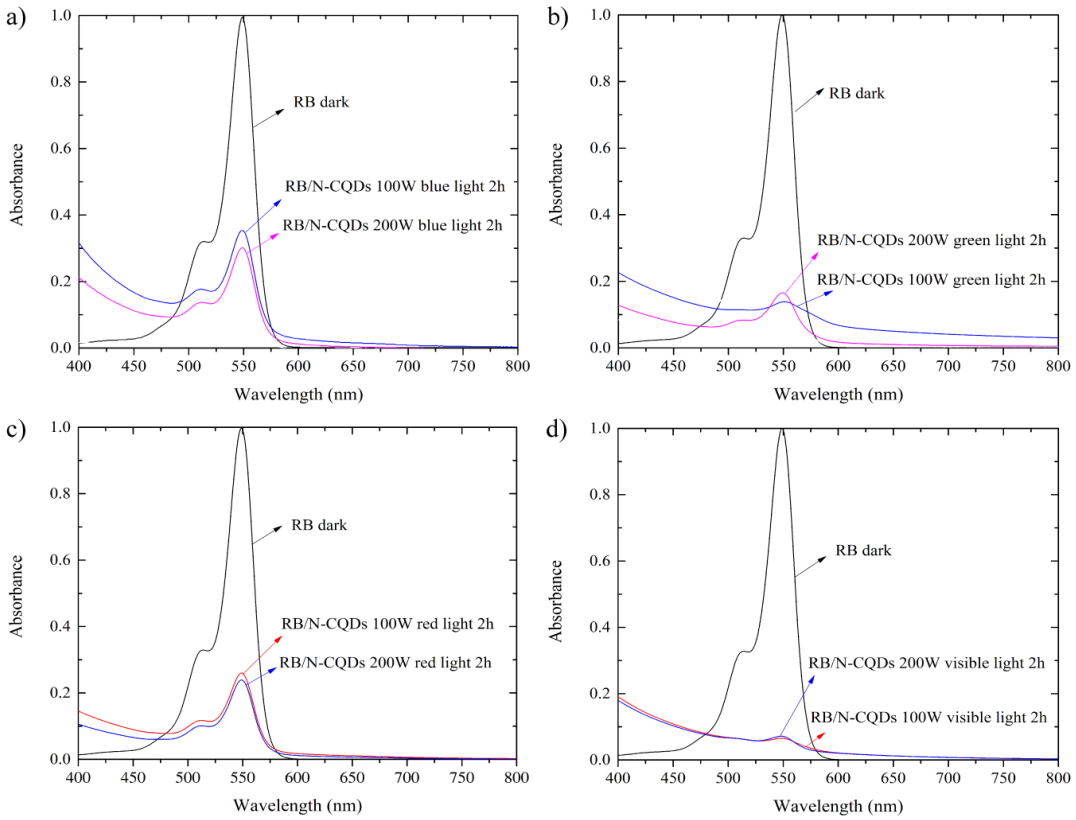


Figure 2. Degradation of RB dye in the presence of N–CQDs samples synthesized under 100W and 200W: a) blue light, b) green light, c) red light and d) visible light.

Table 2. Decomposition percentage of RB under different wavelength irradiations.

Irradiation wavelength (nm)	***N–CQDs 100W Degradation***	***N–CQDs 200W Degradation***
Blue light (380–500 nm)	65%	70%
Green light (500–570 nm)	86%	84%
Red light (625–740 nm)	74%	76%
Visible light (400–700 nm)	93%	94%

Conclusion

Presented study demonstrates the effect of the light irradiation wavelength on the decomposition efficiency of organic dye pollutant such as RB in water medium. The decomposition was examined in the presence of N–CQDs semiconductor photocatalyst with approximately 10 to 11% of attached nitrogen, synthesized by fast and easy method using microwave reactor. Successful decomposition was obtained under every examined wavelength with slight diversity inside the visible range. The highest decomposition efficiency was observed however while irradiating samples containing RB/N–CQDs under visible light comparing to irradiation with separate parts of visible light spectrum.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2020-14/200017).

References

[1]. Chequer FMD, Venâncio V de P, Bianchi M de LP, Antunes LMG. Genotoxic and mutagenic effects of erythrosine B, a xanthene food dye, on HepG2 cells. Food Chem Toxicol. 2012 Oct;50(10):3447–51.

[2]. Mpountoukas P, Pantazaki A, Kostareli E, Christodoulou P, Kareli D, Poliliou S, et al. Cytogenetic evaluation and DNA interaction studies of the food colorants amaranth, erythrosine and tartrazine. Food Chem Toxicol. 2010 Oct;48(10):2934–44.

[3]. Allen MJ, Tung VC, Kaner RB. Honeycomb Carbon: A Review of Graphene. Chem Rev. 2010 Jan 13;110(1):132–45.

[4]. Lee M, Chen B-Y, Den W. Chitosan as a Natural Polymer for Heterogeneous Catalysts Support: A Short Review on Its Applications. Appl Sci. 2015 Nov 17;5(4):1272–83.

[5]. Colmenares JC, Xu Y-J, editors. Heterogeneous Photocatalysis. Berlin, Heidelberg: Springer Berlin Heidelberg; 2016. (Green Chemistry and Sustainable Technology).

[6]. Sun D, Ban R, Zhang P-H, Wu G-H, Zhang J-R, Zhu J-J. Hair fiber as a precursor for synthesizing of sulfur- and nitrogen-co-doped carbon dots with tunable luminescence properties. Carbon N Y. 2013 Nov;64:424–34.

[7]. Hu Y, Yang J, Tian J, Jia L, Yu J-S. Oxygen-driven, high-efficiency production of nitrogen-doped carbon dots from alkanolamines and their application for two-photon cellular imaging. RSC Adv. 2015;5(20):15366–73.

[8]. Prekodravac JR, Jovanović SP, Holclajtner-Antunović ID, Peruško DB, Pavlović VB, Tošić DD, et al. Monolayer graphene films through nickel catalyzed transformation of fullerol and graphene quantum dots: a Raman spectroscopy study. Phys Scr. 2014 Sep 1;T162:014030.

[9]. Prekodravac JR, Marković ZM, Jovanović SP, Holclajtner-Antunović ID, Kepić DP, Budimir MD, et al. Graphene quantum dots and fullerenol as new carbon sources for single–layer and bi–layer graphene synthesis by rapid thermal annealing method. Mater Res Bull. 2017 Apr;88:114–20.

[10]. Jovanović SP, Syrgiannis Z, Marković ZM, Bonasera A, Kepić DP, Budimir MD, et al. Modification of Structural and Luminescence Properties of Graphene Quantum Dots by Gamma Irradiation and Their Application in a Photodynamic Therapy. ACS Appl Mater Interfaces. 2015 Nov 25;7(46):25865–74.

[11]. Saud PS, Pant B, Alam A-M, Ghouri ZK, Park M, Kim H-Y. Carbon quantum dots anchored TiO2 nanofibers: Effective photocatalyst for waste water treatment. Ceram Int. 2015 Nov;41(9):11953–9.

[12]. Liu R, Li H, Duan L, Shen H, Zhang Y, Zhao X. In situ synthesis and enhanced visible light photocatalytic activity of C-TiO 2 microspheres/carbon quantum dots. Ceram Int. 2017 Aug;43(12):8648–54.

[13]. Prekodravac J, Vasiljević B, Marković Z, Jovanović D, Kleut D, Špitalský Z, et al. Green and facile microwave assisted synthesis of (metal-free) N-doped carbon quantum dots for catalytic applications. Ceram Int. 2019;