DEGRADATION OF ORGANIC DYES UNDER VISIBLE LIGHT

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Abstract
We performed the "bottom-up" synthesis of N–doped CQDs *via* swift and easy one–step microwave–assisted method. The percentage of bound nitrogen in this short amount of time was about 11 at% in the form of pyrridinc/NH_2, pyrrolic–N and graphitic–N. The synthesized N–doped CQDs showed good photocatalytic activiti in organic dyes degradation after only 30 min of expoisure to the visible light.

Introduction
The water polution is one of the major problem of today. Industries discharge waste matter, containing organic dyes, into natural water resources without any treatment [1]. These organic dyes, such as rose bengal (RB) and methylene blue (MB) are extrimely genotoxic, mutagenic and cytotoxic [2–6]. So far, various semiconductor materials have been used as photocatalysts for the removal of different dyes from aqueous solutions. Different parameters affect the rate of the dye degradation, such as pH, concentration and light intensity [1]. Here we performed the photocatalytic degradation of RB and MB in the presence of visible light.

Experimental
Synthesis of N–CQDs was performed from water solution of glucose in the presence of ammonia hydroxide (NH_4OH, 25%). Aqueous solution were irradiated in closed−vessel system of CEM Discover BenchMate single mode microwave reactor for only 1 minute, at fixed temperature (100 °C) and power (100 W, 200 W). After synthesis, the samples were dialized for 5 days and filtrated through filters from 450 nm to 10 nm. For the photocatalytic activity study, the N–CQD_{100} or N–CQD_{200} samples were dispersed in RB (0.03 mM) and MB (0.03M) water solutions and treated under visible light at different condditions.

Results and discussion
The Atomic force microscopy (AFM) was used for analysis of morphology and structure of synthesized N–CQDs (Fig 1.) showing that samples (N–CQD_{100} and N–CQD_{200}) have good morphology with spherical like shapes. Taking into account the anomalies related to measurements of particles thickness [7] and diameter [8] we calculated the real particle diameter distribution by analysing 100 dots for each sample. The measured real particle diameters were in the range from 5 to 30 nm.

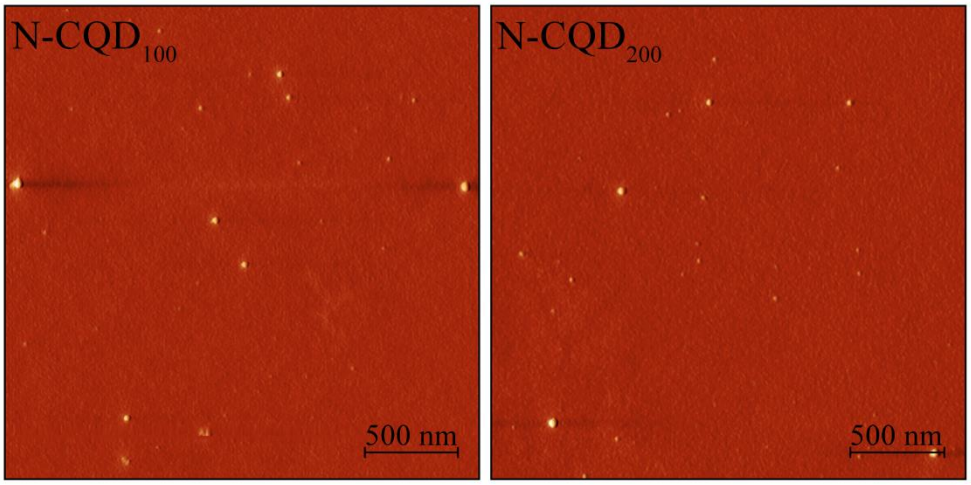

Figure 1. Top view AFM images of N–CQD_{100} (left) and N–CQD_{200} (right) samples.

Chemical analysis of the synthesized N–CQDs was performed with XPS measurements (Table 1). From the XPS results, we noticed that with increase in applied MW power there is the increase in C sp^3 comparing to the sp^2 domains. These results suggest that synthesized quantum dots are carbon nanodots consisting of sp^2 carbon domains in sp^3 carbon matrix. The XPS analysis also showed incorporation of relatively high atomic percentage (at%) up to 10 to 11 at% approximately, of N containing groups in the samples. The highest noticed N at% was in the form of pyridinic/NH_2. The detail analysis of the XPS spectra is presented in Table 1.

Table 1. Detail XPS analysis of the N–CQDs samples.

	Sample N–CQD_{100}		**Sample N–CQD_{200}**	
Name	***Peak BE (eV)***	***Atomic %***	***Peak BE (eV)***	***Atomic %***
C1s sp^2	284.5	18.9	284.5	18.8
C1s sp^3	285.1	22.7	285.1	28.2
N1s pyrrolic	400.4	23.4	400.4	20.8
N1s pyridinic/NH2	399.4	64.6	399.4	69.3
N1s graphitic/NH3+	401.7	12.0	401.6	9.8

Photo degradation rate of RB and MB under visible light was examined by changing the catalyst concentration (0.25 mg/ml and 1 mg/ml) and irradiation time (30 min to 24h). Fig. 2 presents the photodegradation rate of RB (%) depending on catalyst concentration and irradiation time. From Fig 2 it can be seen that the degradation rate increases with increase in the catalyst concentration from 72–78 % at lower concentration to 92–93 % at higher catalyst concentration. The influence of the irradiation time was the most obvious after 30 min of exposure to the visible light while further prolongation of irradiation time did not had any significant effect on the dye degradation rate.

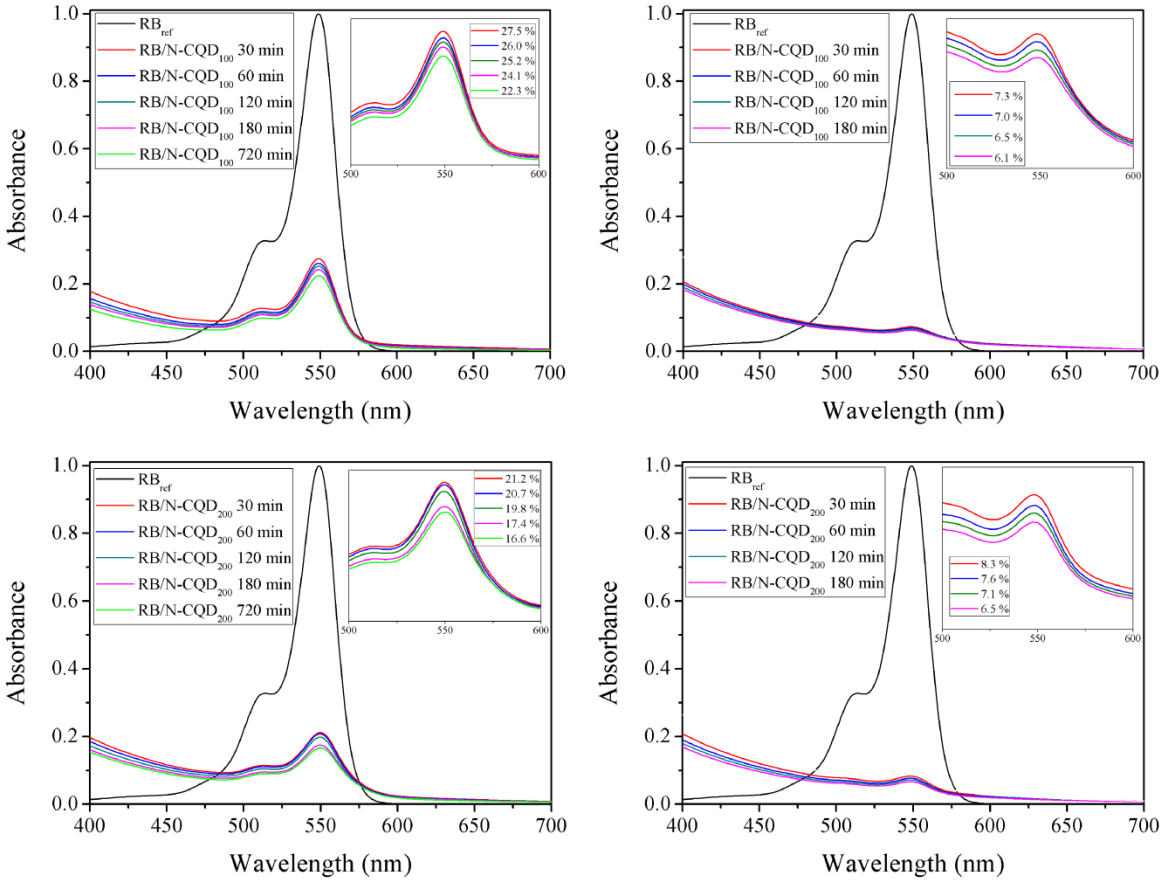

Fig 2. The dye degradation rate of RB (%) depending on the catalyst concentration of 0.25 mg/ml (left) and 1 mg/ml (right) and irradiation time (from 30 to 720 min).

Fig 3. presents the degradation rate of MB (%) after 4h and 24h of the exposure to the visible light.

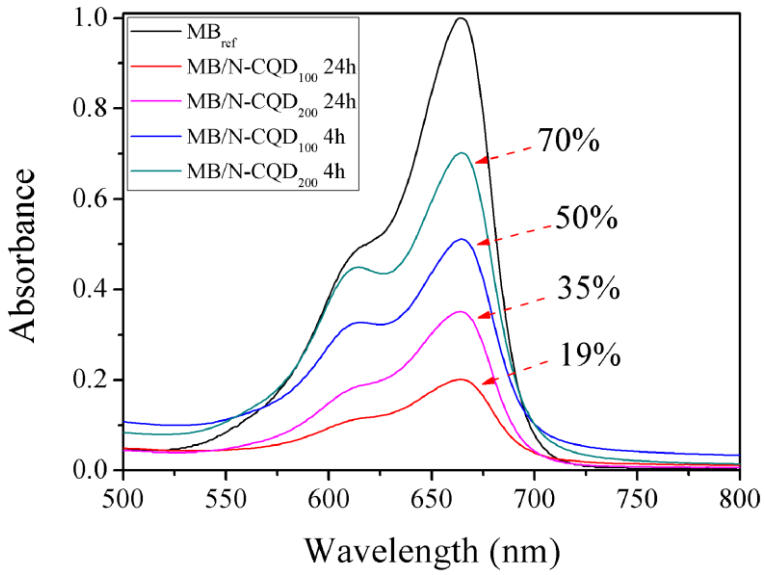

Fig 3. MB degradation rate (%) depending on irradiation time.

Here can be seen that the degradation rate is smaller comparing to the results obtained for RB degradation. After 4h of exposure to the visible light almost 50 to 70% of MB remain in the

samples, while after 24h of exposure the degradation rate was up to 70 to 80%. Smaller concentrations than 1 mg/ml were not examined since at this catalyst concentration results showed that at least 24h are necessary for significant degradation.

Conclusion

Here we demonstrated fast and easy one–step microwave assisted synthesis of N–doped carbon quantum dots with approximately 10–11 % of attached nitrogen. The photocatalytic activity of synthesized N–doped CQDs as catalyst was examined on the RB and MB toxic organic dyes. Very good degradation rate of RB up to 93 % was proven after only 30 min of exposure to the visible light irradiation, where further prolongation of irradiation time did not affect significantly on the RB degradation. By examining the effect of catalyst concentration, we noticed that the degree of RB degradation increases proportionately with increasing catalyst concentration. By analysing the degradation of MB we observed the significant degradation rate after 24h of exposure to the visible light. The obtained results indicate the possibility of using synthesized material for purification of textile industry wastewaters.

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