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Lecture Proceedings

ANTIOXIDANT AND PROOXIDANT FEATURES OF N-CQD IN PHOTOCATALYTIC TESTING OF AQUATIC MEDIA

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Abstract
The modern age science is still searching for an effective photocatalytic material for the treatment of colored discharges from different industries which cause severe environmental issues. The excellent properties of nitrogen doped carbon quantum dots (N-CQD) enable their successful application as photocatalytic material in organic dye removal triggered under light absorption. With this in mind we first present a successfully performed microwave-assisted synthesis method, a green, simple and economically affordable method for N-CQD synthesis with high nitrogen percentage incorporated in the form of pyrrolic, pyridinic/NH_2 and graphitic/NH_3^+ groups. The pro-oxidant and antioxidant features of the synthesized N-CQD were further presented, with high removal efficiency of synthesized N-CQD towards the methylene blue (MB) organic dye, as one of the leading water pollutants with a major risk to aquatic and human life.

Introduction
The MB dye, is extremely dangerous with strong effect on human beings as well as on the environment [1–3]. Efforts for removal of organic toxic dyes from natural sources, through adsorption or in the presence of photoactive materials, over the years caught significant research attention [4,5]. Due to ease functionalization, optical properties and high stability upon irradiation, CQD found application in treatment of different pollutants [6]. N-doped CQD are interesting carbon nanoparticles with particle sizes less than 10 nm and outstanding photo-luminescent properties. The presence of oxygen containing functional groups provides a good solubility of N-CQD in water media allowing their application as photocatalyst in organic dyes treatment.
Guided by the idea that 25% of sunlight is actually a blue light, we explored the time dependent photoactivity of N-CQD towards removal of MB dye from water under blue light irradiation (470 nm). Apart from efficient production of hydroxyl radicals (•OH), we discovered the potential antioxidant activity of synthesized N-CQD.

Experimental
The N-doped CQD were synthesized using green precursor and microwave assisted method as described previously [7]. The antioxidant potential of N-CQD was measured using DPPH•. The freshly prepared methanol solutions of DPPH• was mixed with different concentrations of N-CQD (20–200 μM) water solution in total volume of 1200 μl. Samples were incubated for 30 min in dark at room temperature, followed by monitoring of the DPPH• absorption at 515 nm by UV-Vis absorption spectrometry. Evaluation of the antioxidant activity of N-CQD examination by $KMnO_4$ reduction assay was performed following the protocol from Ruiz et. al [8]. After incubation in dark conditions for 1h, the change in the absorption intensity of charge transfer transitions at 506, 525, 545 and 566 nm, along with the solution color change was monitored. The prospect of hydroxyl radicals (•OH) to be the ROS in charge for removal of

MB organic dye was examined using the test with terephthalic acid (TPA) by photoluminescence (PL) [7].
The MB removal efficiency in the presence of the N-CQD photocatalyst was examined in batch under blue light irradiation (470 nm). The reaction mixture containing 20 ml of MB stock solution (0.03 mM) in the presence of a photocatalyst the N-CQD (0.25 mg/ml) was exposed to irradiation in black box conditions to avoid the influence of the external light. Samples were placed directly on the free-standing lamp with free surface area of 28 cm^2 and irradiation power of 3 W, followed by irradiation in different time intervals 120, 180, 240 and 300 min. The removal efficiency was monitored by decrease in the absorption band maximum at 664 nm characteristic for MB dye.

Results and discussion

The N-doped CQD received attention from the research community with regard to their pro- and antioxidant activity. As 0D nanomaterials, the CQD are known as both electron donors and acceptors. Hence, along with the ability to generate ROS under UV-Vis light irradiation they express an antioxidant activity as well [9].
The capacity of N-CQD to produce hydroxyl radicals was tested using luminescent molecule such as TPA. The TPA reacts with •OH forming highly fluorescent product HTPA under irradiation. The PL peak intensity of the HTPA is proportional to the amount of produced •OH radicals. In Figure 1 we present the PL intensity change of suspension containing N-CQD photocatalyst and TPA transformation into hydroxylated HTPA form. No peak was noted in the absence of the photocatalyst, while the presence of N-CQD photocatalyst promoted the reaction of TPA with •OH radicals on the photocatalyst-water interface.

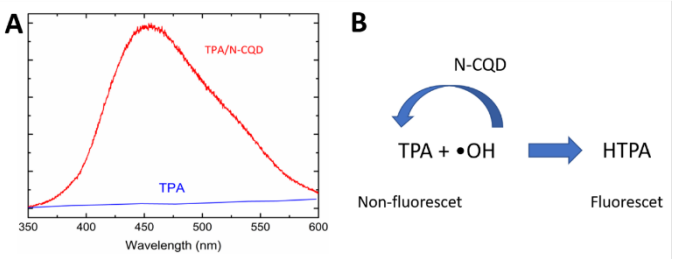

Figure 1. The pro-oxidant activity of N-CQD using TPA test (A) and the TPA transformation into fluorescent form HTPA the presence of N-CQD (B).

The antioxidant potential of CQD has been proven previously using DPPH as most common free radical for evaluation of N-CQD scavenging activity (Figure 2) [8]. The Vit. C with high scavenging activity for reactive oxygen species in the same concentration range was used as a control (Figure 2B). Results for control Vit. C showed the increasing activity at concentrations up to 80 µg/ml followed by saturation effect, while the sample N-CQD showed only moderate efficiency bellow 80 µg/ml. The actual scavenging activity increase was observed for concentration 100 to 200 µg/ml. Further increase in the concentration would lead to saturation effect (Figure 4D). Observation was followed by the color change from purple to yellow. The estimated amount of antioxidant necessary to decrease the concentration of DPPH by 50 % was calculated to be 33.11 µg/ml for Vit. C, while for the N-CQD the value of 177.82 µg/ml showed five times lower efficiency comparing to control (Figure 2C).

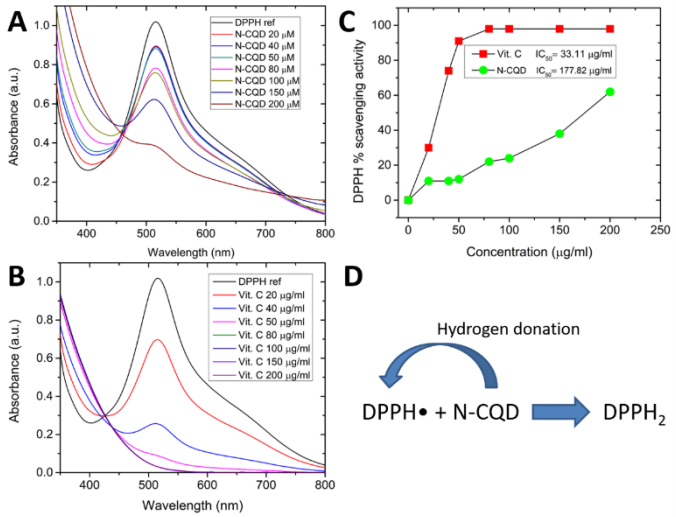

Figure 2. The scavenging activity of N-CQD (A) and control Vit. C (B) against DPPH free radical; the calculated IC_{50} for both set of samples (C), and DPPH• transformation into its stable form $DPPH_2$ in the presence of N-CQD (D).

The evaluation of the oxide radical scavenging activity of N-CQD with the $KMnO_4$ reduction assay is presented in Figure 3A. Following the obvious decrease in the characteristic $KMnO_4$ band intensity at 506, 525, 545 and 566 nm by adding N-CQD to the $KMnO_4$, the spectral changes confirmed reduction of Mn^{7+} to Mn^{2+}. At a concentration of 0.04 mg/ml for N-CQD, a strong decrease in absorption of over 93 % was observed followed by saturation effect above 0.06 mg/ml. Comparable results were obtained for control experiment in the absence of N-CQD using ascorbic acid (Vitamin C – Vit. C) as standard (Figure 3B). The obtained IC_{50} value for sample set with N-CQD was 0.02 mg/ml, while for control experiments in the presence of Vit. C the IC_{50} value was comparable (0.01 mg/ml), suggesting the extraordinary antioxidant activity of N-CQD (Figure 3C). The high sp^2 to sp^3 ratio 18.9 at% to 22.7 at% in synthesized N-CQD stimulate the electron transfer from N-CQD to $KMnO_4$ promoting the reduction.

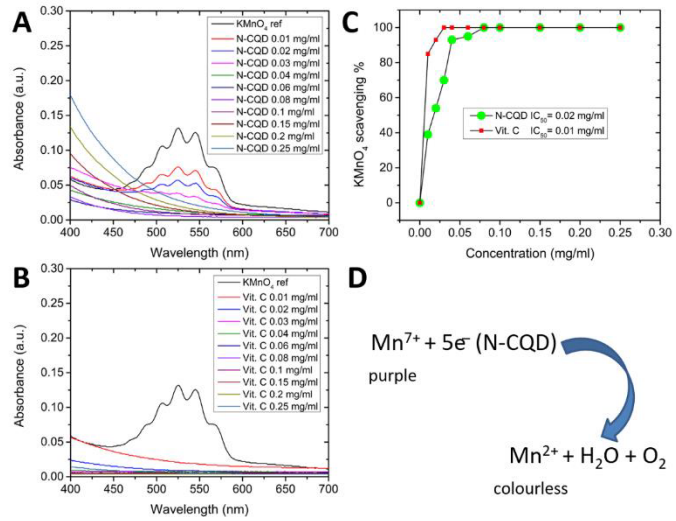

Figure 3. The $KMnO_4$ reduction assay of: N-CQD (A) and control Vit. C (B); calculated IC_{50} values for both set of samples (C), and $KMnO_4$ reduction to colorless Mn^{2+} in the presence of N-CQD (D).

Organic dye MB, as a member of phenothiazine family, possess a heterocyclic aromatic chemical structure with three combined aromatic rings and C–S, CN and CN= functional groups. As a water soluble molecule, it can slowly degrade in aqueous media due to •OH produced from water becoming active upon irradiation [6]. The MB removal process started in the presence of synthesized N-CQD in dark conditions (14 %) as a result of the MB dye adsorption on N-CQD high surfaces contact area (Figure 4A). After switching on the irradiation source, the removal efficiency of the synthesized N-CQD photocatalyst increased exponentially with time as shown in Figure 4B. Under blue light irradiation, the MB removal process became faster in the presence of N-CQD as photocatalyst indicating their strong influence on the photocatalytic activity. This is due to the fact that N-CQD possess unique lone pair states that are contributed by nitrogen atoms, which affects their band gaps leading to formation of new energy levels in between the conduction and the valence bands [10].

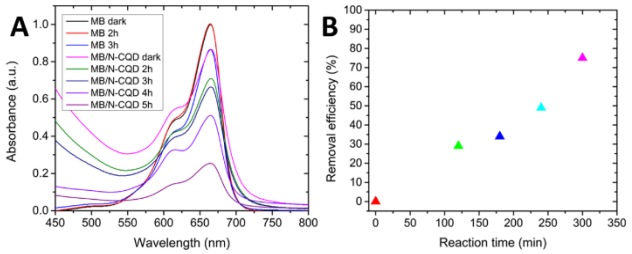

Figure 4. The photocatalytic test results (A), and the N-CQD removal efficiency percentage towards MB dye against irradiation time (B).

Upon irradiation of N-CQD, the hydroxyl radical species (˙OH) can be generated. Therefore, the degradation of MB dye goes preferably through decomposition of the chromophore structure and the destruction of the homo and heteropoly aromatic rings of MB molecule [11]. The initial step of MB degradation is cleavage of the bonds of the C–S^+=C functional group in MB dye molecule [12]. The adsorption of MB dye onto photocatalyst leads to interaction of the generated OH• radicals with C–S^+=C functional group in cationic dye. In order to maintain double bond conjugation, the central aromatic ring, containing S and N atoms, will open. Further attack of reactive radical species leads to dissociation of the two benzene rings into intermediate products, whose successive hydroxylation further leads to the aromatic ring opening and finally to the conversion of organic carbon into harmless gases [6].

Conclusion

The presented research showed the green, easy and fast microwave assisted method for production of N-doped CQD from a glucose precursor. Synthesized N-CQD, at low concentration of only 0.25 mg/ml, showed remarkable removal efficiency towards MB dye under blue light irradiation. In contribution, the high percentage of nitrogen, in the form of amino groups or incorporated in the basal plane of N-CQD, resulted in synthesis of electron-rich structures, with oxide radical scavenging activity to be expected. By increasing the photocatalyst concentration and fine-tuning of the reaction media, the MB dye adsorption onto the N-CQD free surface can be promoted. Consequently, the reduction of irradiation time needed for the same removal rate is expected, which opens the possibilities to further expand the research focus.

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