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ARTICLE TYPE

B-doped carbon quantum dots as a sensitive fluorescence probe for hydrogen peroxide and glucose detection

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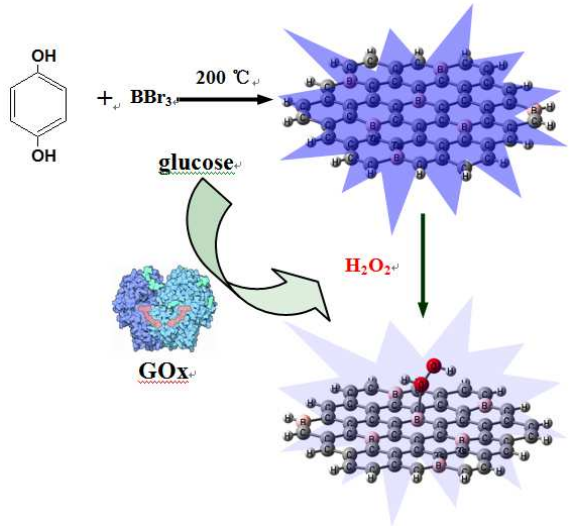
Fluorescent B-doped carbon quantum dots (BCQDs) were prepared by a facile one-pot solvothermal route. The BCQDs can be used as a novel fluorescence sensing system for hydrogen peroxide and glucose detection.

Carbon quantum dots (CQDs) have been attracting much attention from various areas including sensor, bioimaging and catalysis due to their outstanding optical and electronic properties.[1-3] A great effort has been devoted to fabrication and property-tuning of pristine CQDs which contain only carbon and oxygen atoms. Although it has proved that pristine CQDs possess good biocompatibility and high resistance to photobleaching, their low quantum yields (less than 10%) with respect to inorganic semiconductor quantum dots and organic dyes considerably limit their broad applications.[4,5] To overcome this drawback, surface modification with polymers or small organic molecules was performed to achieve high fluorescence efficiency.[6-9] Recent studies showed element-doping such as nitrogen-incorporating can greatly enhance the fluorescence of doped CQDs with quantum yield of more than 20%.[10-12] However, the doping of other elements such as boron into CQDs still remains unclear to date.

Excellent photoluminescence of CQDs resulted from surface modification and element-doping, and their good biocompatibility provide promising prospect for application in biodetection and biosensor, especially in glucose sensors. Zheng et al.[13] took advantage of peroxidase-like catalytic activity of CQDs to achieve the colorimetric detection of H_2O_2 and glucose. Similar glucose sensor was reported by Liu et al.[14] using N-doped CQDs. Both studies demonstrated the quantification of glucose was achieved by monitoring the coloration of TMB induced by oxidation of hydrogen peroxide. Qu et al.[15] synthesized phenylboronic acid functionalized CQDs and constructed a carbon dots-based selective and sensitive sensing system for glucose. Li et al.[16] employed CQDs and a boronic acid substituted bipyridinium salt to build a fluorescence assay for glucose detection, which is realized via fluorescence quenching by the salt and subsequent recovery by glucose. These two studies involved the complex functionalization of CQDs with boron-containing compounds to realize the sensing purpose. Herein, we report a novel fluorescence sensing system for hydrogen peroxide and glucose detection based on the boron-doped carbon quantum dots (BCQDs) without further functionalization, which was synthesized through one-opt solvothermal route for the first time. As shown in Scheme 1, taking advantage of selectively strong fluorescence quenching ability of hydrogen peroxide to BCQDs, a new detection strategy based on BCQDs for hydrogen peroxide, and an assay system for glucose detection based on glucose oxidase (GOx) and BCQDs were developed without chemical modification of BCQDs. The detection limit for glucose is as low as 8.0 μM, satisfying the requirement for real sample determination in microdialysate.[15]

A facile one-pot solvothermal route is employed to fabricate BCQDs by employing BBr_3 as the boron source and hydroquinone as precursor.[17] A great deal of boron atoms were incorporated into carbon dots. The as-prepared BCQDs were dialyzed to remove the extra original compounds. The transmission electron microscopy (TEM) image in Fig. 1A showed the average size of BCQDs is about 16 nm and they span widely from 8 nm to 22 nm in size. High transmission electron microscopy (HRTEM) image in Fig 1b depicted that large particles in Fig 1a are from assembly of smaller nanodots which are about 5 nm in size, close to those of CQDs without doping in reference.[18] The HRTEM image also demonstrated the graphene-like crystalline structure of BCQDs, the spacing of adjacent lattice planes spans from 2.0 to 2.4 Å, obviously different from CQDs from graphite.[19,20]



Scheme 1. Schematic representation of synthesis of BCQDs and glucose-sensing mechanism based on BCQDs and H_2O_2

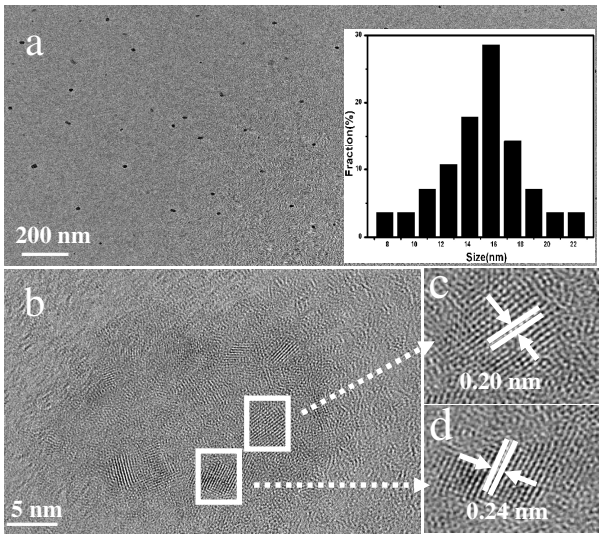


Fig. 1 The TEM image of BCQDs (a) and HRTEM image of BCQDs (b, c and d). Inset: size distribution.

Table 1 Concentration of C, O, B and Br (Cl) in the carbon dots samples as determined by XPS

Samples	C (wt. %)	O (wt. %)	B (wt. %)	X[c] (wt. %)
BCQDs[a]	69.4	21.0	5.9	3.6
CQDs [b]	67.8	26.8	-	5.4

[a] BCQDs was prepared using BBr_3 and hydroquinone. [b] CQDs was prepared using CCl_4 and hydroquinone from Ref. 17. [c] X represents Br for BCQDs, and Cl for CQDs respectively.

The BCQDs mainly consist of carbon, oxygen, boron and bromine as shown in Fig. S1. The XPS survey spectrum of BCQDs shows a predominant C1s peak at ca. 284.8 eV, and an O1s peak at ca. 533.3 eV, a B 1s peak at ca. 194.3 eV and a Br 3d peak at ca. 68.7 eV. The peak of B1s at 194.3 eV in Fig S1 can be assigned to B-O bond according to the reference.[21-23] In Fig S1c, C 1s core level peaks appeared at 283 eV, 284.7 eV, 286 and 287.5 eV which are assigned to the oxygen components in C-B, C=C, C-O and C=O bonds.[21-23] These XPS results confirmed the incorporation of B atoms into the CQDs. The quantitative determination by XPS in Table 1 showed that BCQDs are composed of 69.4% carbon, 21.0% oxygen, 5.9% boron and 3.6% bromine in weight, while CQDs have similar composition except for the absence of boron.

BCQDs exhibit bright blue fluorescence both in water and ethanol under the UV light, whereas CQDs show weak green light as shown in Fig. 2 inset. Fig. 2 depicted that BCQDs show a strong fluorescence emission peak at 368 nm, while CQDs have the emission band at 440 nm. The large blue shift of emission for BCQDs with respect to CQDs may be attributed to strong electron-withdrawing ability of boron, which is reported to be between –CN and $–NO_2$,[24] because boron is a well-known electron-deficient Lewis acid. The fluorescence quantum yield of BCQDs is up to 14.8%, much higher than that of CQDs (3.4%). Quantum yields in Table S1 suggested the boron-enhancement of fluorescence for BCQDs relative to CQDs since boron can act as an engine for charge transfer especially in the excited state. Similar boron-enhancement of

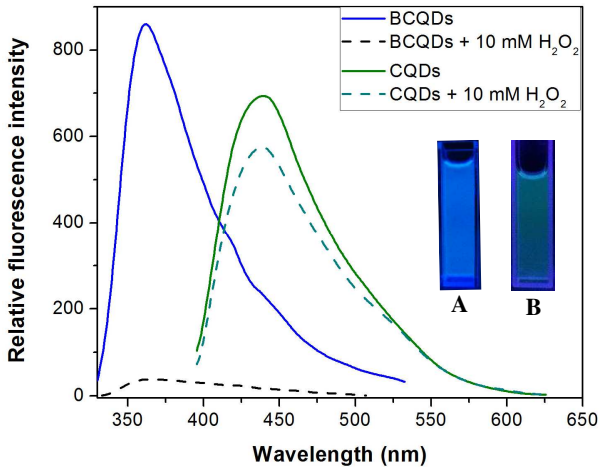


Fig. 2 Fluorescence spectra of BCQDs and CQDs, and effect of H_2O_2 on fluorescence of BCQDs and CQDs. Inset: photographs of BCQDs and CQDs under UV light.

fluorescence was also found in the boron-containing compounds.[24] It is interesting that fluorescence of BCQDs can nearly completely be quenched by H_2O_2 whereas only very small influence can be observed for CQDs. Electron-transfer mechanism was proposed to explain the quenching of CdTe QDs and SiQDs by H_2O_2. For the CdTe QDs, it is assumed that electron-transfer reaction between QDs and H_2O_2 leads to O_2 which lies in electron/hole traps on QDs resulting in the fluorescence quenching.[25] For SiQDs, it is presumed that active oxygen species of H_2O_2 can capture electrons at the conduction bands of SiQDs and thus inhibit the radiative recombination of photoinduced electrons and holes.[26] However, the quenching effect of O_2 on BCQDs can be negligible relative to that of H_2O_2 as shown in Fig. S4, indicating that oxygen produced by H_2O_2 is not responsible for strong fluorescence quenching. Thus, it is reasonably deduced that considerable charge transfer between H_2O_2 and boron in BCQDs leads to the fluorescence quenching because H_2O_2 can donate electron to boron atoms with high electron-deficiency forming stable B-O coordination bond, suggesting boron as an electron acceptor plays a key role in this phenomenon induced by charge transfer mechanism.

The capability of BCQDs-based sensing system for detection of H_2O_2 and glucose were evaluated under

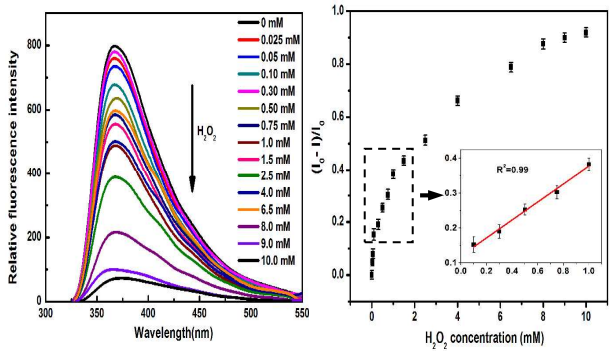


Fig. 3 The fluorescence response of BCQDs with respect with H_2O_2 concentration. a) The change in emission spectra. b) The change in quenching efficiency $(I_0\text{-}I)/I_0$, where I_0 and I are fluorescence intensity of BCQDs without and with H_2O_2. Inset: The linear response of quenching effect $(I_0\text{-}I)/I_0$ of BCQDs vs. H_2O_2 concentration from 0.1 to 1.0 mM.

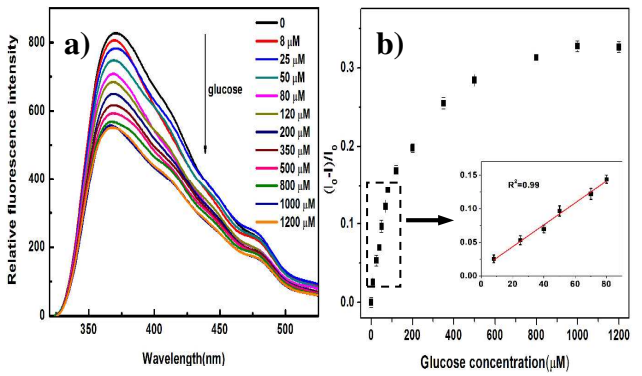


Fig. 4 The fluorescence response of BCQDs vs. glucose concentration with aid of GOx. a) The change in emission spectra. b) The change in quenching efficiency $(I_0-I)/I_0$, where I_0 and I are fluorescence intensity of BCQDs without and with H_2O_2. Inset: The linear response of quenching effect $(I_0-I)/I_0$ of BCQDs vs. H_2O_2 concentration from 8.0 to 80.0 μM.

the optimum conditions (Figure S5 and S6). The fluorescence response of BCQDs to H_2O_2 concentration is shown in Fig. 3. The fluorescence intensity gradually decreases as increasing H_2O_2 concentration, while the fluorescence quenching efficiency shows successive growth with respect to H_2O_2 concentration. The fluorescence quenching efficiency is linearly correlated with H_2O_2 concentration from 0.1 to 1.0 mM and retains constant when H_2O_2 concentration is higher than 10.0 mM. The quenched fluorescence can be recovered in the presence of MnO_2 (Fig S7). It has been proven that glucose oxidase (GOx) can be utilized to catalyze the oxidation of glucose to release gluconic acid and H_2O_2.[27,28] The sensitive detection of H_2O_2 enables BCQDs to construct sensing system for glucose with aid of GOx. Thus, the sensing system consisting of BCQDs and GOx was assessed to detect glucose at pH 7.4. Fig. S8 demonstrated the fluorescence can not respond to single glucose or GOx but can be largely quenched by their combination. The fluorescence quenching of BCQDs was observed with increasing glucose concentration in the presence of GOx. Fig. 4 depicted the fluorescence can be continuously quenched by addition of glucose in a large concentration range of 1000.0 μM. The sensor exhibited an excellent linear response to glucose concentration ranging from 8.0 to 80.0 μM with a detection limit of 8.0 μM, much lower than those of other CQDs-based fluorescence sensors.[15,16]

In summary, we successfully synthesized B-doped carbon quantum dots by a facile one-pot method, and revealed the doping of boron into carbon quantum dots can largely enhance the fluorescence. Taking advantaging of effective fluorescence quenching effect of hydrogen peroxide induced by charge transfer between doped boron atoms and hydrogen peroxide, a sensitive BCQDs-based fluorescence analytical system for hydrogen peroxide was established. With the aid of glucose oxidase, quantitative detection of glucose with high sensitivity and selectivity was achieved based on BCQDs fluorescence platform.

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Notes and references

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† Electronic Supplementary Information (ESI) available: XPS, fluorescence specra and experimental details. See DOI: 10.1039/b000000x/

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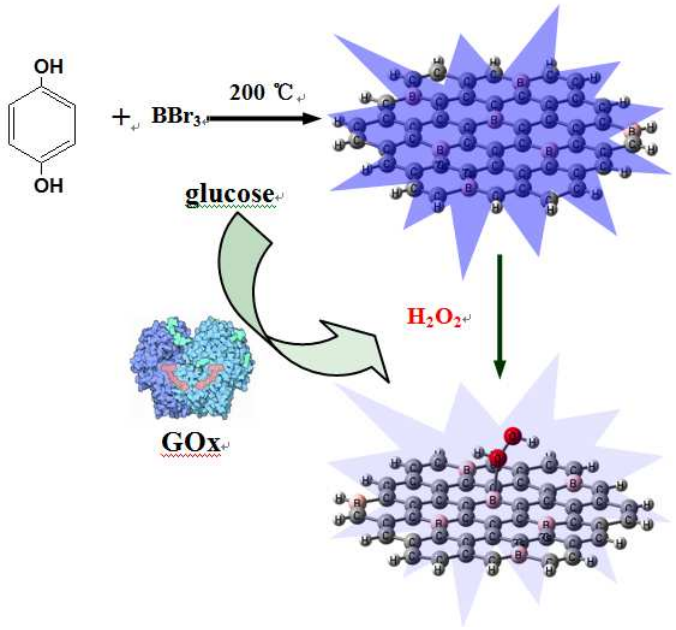
Graphical Abstract

B-doped carbon quantum dots as a sensitive fluorescence probe for hydrogen peroxide and glucose detection

Xiaoyue Shan, Rujing Chai, Juanjuan Ma, Zhaosheng Qian, Jianrong Chen and Hui Feng*



Fluorescent B-doped carbon quantum dots (BCQDs) were used as a novel fluorescence sensing system for hydrogen peroxide and glucose dectection.