3-Aminobenzeneboronic acid functionalized MoS$_2$ quantum dot as fluorescent nanoprobe for the determination of o-dihydroxybenzene

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Abstract

In this work, by functionalizing MoS$_2$ quantum dot with 3-aminobenzeneboronic acid, a novel multifunctional quantum dots (denoted as B-MoS$_2$ QD) was obtained and used successfully as fluorescence nanoprobe for detecting o-dihydroxybenzene (o-DHB). Transmission electron microscopy, fluorescence spectrum, UV-vis spectrum and fluorescence lifetime were used to investigate the prepared nanoprobe. The results show that the B-MoS$_2$ QD nanoprobe can exhibit strong fluorescence and excellent light fastness owing to the coupled effect from the MoS$_2$ QDs and boronic acid; interesting, the vicinal diols structure from its surface can bridge covalently with o-DHB, resulting that the fluorescence quenching of B-MoS$_2$ QD and selective recognition toward o-DHB. With the increasing of o-DHB concentration, the nanoprobe fluorescence would gradually decrease. By measuring the fluorescence intensity of B-MoS$_2$ QD, a wide linear range from 0.1 μM...
to 200.0 μM with a low detection limit of 0.025 μM were obtained for o-DHB analysis; meanwhile, this fluorescence nanoprobe possesses excellent selectivity, which can selective detect o-DHB from its analogues.

**Keywords:** o-Dihydroxybenzene; Fluorescence; Quantum dots; MoS$_2$; Nanoprobe.

**Introduction**

o-Dihydroxybenzene (o-DHB) is an important intermediate material and used widely in the fields of medicine, pesticide and dyestuff. Meanwhile, o-DHB is also a major phenolic pollutant with high toxicity, and it is extremely harmful to the ecological environment and human body.$^{1-4}$ thus the sensitive and selective detection of o-DHB is very important.$^5,6$ In recent years, many methods such as high-performance liquid chromatography,$^7,8$ electrochemistry,$^9,10$ electrogenerated chemiluminescence,$^{11}$ and optical sensing$^{12}$ have been developed for o-DHB detection. These methods are very important, while most of these methods are expensive, time-consuming and hard to differentiate o-DHB from its analogues including m-dihydroxybenzene (m-DHB) and p-dihydroxybenzene (p-DHB). Generally, o-, m- and p-DHB coexist in the same system and interfere with each other during the determination resulted from their similar characteristics, structures, and physiochemical property,$^{13}$ hence it is very urgent to develop an effective method with high selectivity for detecting o-DHB.

One kind of typical graphene-analogous two-dimensional inorganic materials, transition metal chalcogenide MoS$_2$ possesses excellent catalytic, electronic and optical properties. Currently, MoS$_2$ nanosheets have been widely used in many fields, such as electrical, hydrogen evolution, and electrochemical.$^{14-18}$ However, there is only a few reports focused on the optical properties of MoS$_2$.$^{19}$ In addition, compared to the two-dimensional MoS$_2$ nanosheets, MoS$_2$ quantum dots (MoS$_2$
QDs) possesses a particle size of less than 10 nm, which directly lead to the unique and extra optical properties for stronger quantum confinement.\textsuperscript{20-23} These characteristics make MoS\textsubscript{2} QDs have outstanding advantages in the field of optical sensing.\textsuperscript{24-27} Obviously, MoS\textsubscript{2} QDs is a desirable candidate for constructing optical sensing assay for o-DHB.

However, using only pure MoS\textsubscript{2} QDs to fabricate optical sensing assay is not desirable. The requirement in an effective sensing assay is not only the presence of the high responsive signal but also one function distinguishing selective target from its interferents.\textsuperscript{28,29} Owing to the ability to bond covalently to vicinal diols, some recent reports demonstrated that boronic acid and its derivatives can exhibit excellent selectivity and sensitivity for vicinal diols structure. In addition, when fluorophore is attached by boronic acid group, its emission would be changed.\textsuperscript{30-32} These interesting properties make boronic acid an ideal tool for developing optical nanoprobe to detect selective o-DHB from its analogues.

On the basic of the above statements, in this study, 3-aminobenzeneboronic acid (APBA) functionalized MoS\textsubscript{2} quantum dots (B-MoS\textsubscript{2} QDs) was synthesized firstly through amidation reaction between APBA and MoS\textsubscript{2} QD, and then, the produced B-MoS\textsubscript{2} QDs was used to construct a novel fluorescence sensor for detecting o-DHB. Scheme 1 depicted the working principle of the fluorescence nanoprobe: the ortho-diol structure of B-MoS\textsubscript{2} QDs can react with the o-hydroxyl of o-DHB to form a large borate ester, which results that the fluorescence of B-MoS\textsubscript{2} QDs is quenched. The B-MoS\textsubscript{2} QDs nanoprobe has a good sensitivity and selectivity toward o-DHB in both aqueous solution and real tap water and lake water. It is confirmed that the developed fluorescence nanoprobe in this work has important application for o-DHB analysis.

**Experiment section**

*Reagents and chemicals*
Sodium molybdate dihydrate (Na$_2$MoO$_4$.2H$_2$O), APBA, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), glucose and other phenolic compounds containing bisphenol A (BPA), phenol (PH), hydroquinone (HQ), o-DHB, m-DHB and p-DHB were supplied by Aladdin Industrial Co. Ltd. (Shanghai, China). All chemicals are of analytical grade and used without any further purification.

**Apparatus**

The fluorescence spectrums were measured with F-7000 Spectrofluorometer (Shimadzu, Japan). UV–Vis absorption spectra were carried out on UV–Vis 2600 spectrophotometer (Shimadzu, Japan). Fourier transform infrared spectroscopy was tested by Nicolet 6700 FT–IR spectrometer (Thermo Fisher Scientific, USA). X-ray photoelectron spectroscopy was measured on a K-Alpha 1063 (Thermo Fisher, U. K.). Transmission electron microscopy (TEM) was obtained using a JEM-3010 (Joel, Japan). The fluorescence lifetime was acquired by Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometer (Horiba, Japan). Purification of MoS$_2$QDs was performed using a centrifuge 5804 R (Eppendorf, Germany).

**Preparation of the B-MoS$_2$ QDs**

Before preparing B-MoS$_2$ QDs, MoS$_2$ QDs was prepared through a one-step hydrothermal method. In brief, 0.121 g of Na$_2$MoO$_4$.2H$_2$O was dissolved in 12.5 mL of ultrapure water. After sonication for 5 min, the solution was adjusted to pH = 6.5 with 0.1 M HCl. Then, 0.25 g of glutathione and 25.0 mL of ultrapure water were added to the solution. After ultrasonication for 10 mins, the mixture was then transferred into a 50.0 mL Teflon-lined stainless-steel autoclave and treated hydrothermally for 36 h at 200°C.

For synthesizing B-MoS$_2$ QD, 10.0 mL of MoS$_2$ QD solution was mixed with 10.0 mL of phosphate buffered solution (PBS) (pH 7.4, 0.2 M). Then, 0.0548 g of APBA and 0.0805 g of EDC
were added to the mixture solution stirring vigorously for 3 h in the dark at room temperature. Finally, the B-MoS$_2$ QD was purified through filtering with a 0.22 μM microporous membrane and stored the filtrate in the refrigerator at 4 °C.

Detection of o-DHB

5.0 μL of B-MoS$_2$ QD and different concentrations of o-DHB were added into 400.0 μL PBS (pH 8.0, 0.1 M), and the mixed solution was incubated for 22 min at 37 °C. Next, the fluorescence emission spectra were recorded for sensing o-DHB. For comparison, the detection for other analytes (1 mM) was carried out via a similar procedure. Tap water (from Lab), and lake water (from YuDai Lake, Jiangsu University) samples were used to real sample detection. These samples were centrifuged and diluted 10 times with PBS buffer solution (pH 8.0, 0.1 M). The final samples were added with different concentration of o-DHB (5.0 μM, 10.0 μM and 20.0 μM ), the real sample detection was carried out using the procedure described above.

Result and discussion

Characterization of B-MoS$_2$ QDs

The microstructure and morphology of B-MoS$_2$ QDs and MoS$_2$ QDs were illustrated via TEM. As shown in Fig. 1, the prepared MoS$_2$ QDs through one-step hydrothermal method has uniform morphology and the average diameter of MoS$_2$ QDs is ~2.2 nm. As for B-MoS$_2$ QDs, the size increases and the diameter is ~2.3 nm which is close to the MoS$_2$ QDs. FT-IR spectroscopy was used further to characterize MoS$_2$ QDs and B-MoS$_2$ QDs (Figure S1). For MoS$_2$ QDs, the strong peaks at 3400 cm$^{-1}$ and 1645 cm$^{-1}$ can be ascribed to N-H stretching vibration and N-H bending vibration, respectively, and the peak at 480 cm$^{-1}$ is ascribed to Mo-S vibration.$^{34}$ As for B-MoS$_2$ QDs, there are three new peaks appeared at 1037 cm$^{-1}$ (B-O-H vibration), 1090 cm$^{-1}$ (C-B stretching vibration), 1135 cm$^{-1}$ (B-O vibration).$^{35, 36}$ The surface elements and chemical composition of
B-MoS$_2$ QDs were investigated with X-ray photoelectron spectroscopy (XPS) spectrum (Fig. 2). It’s noted from Figure 2A that the B-MoS$_2$ QDs possesses six peaks which are corresponding to Mo, S, N, C, O and B, wherein B peak is not existed in MoS$_2$ QDs, implied that the boronic acids group modified the surface of MoS$_2$ QDs. Fig. 2B shows that the Mo 3d spectrum is deconvoluted into three peaks located at 226.8, 228, 231.8 eV, which are corresponding to S 2s, Mo 3d$_{5/2}$, Mo3d$_{3/2}$, respectively. From Fig. 2C, it can be found that the S 2p spectrum displayed S 2p$_{3/2}$ and S 2p$_{1/2}$ at 163 eV$^{-1}$ and 164 eV$^{-1}$, respectively, and the other two peaks in the spectrum are belong to S$_2$O$_3^{2-}$ group. In Fig. 2D, the B 1s spectrum shows two peaks appear at 191.0 eV$^{-1}$ for B-C, 191.9 eV$^{-1}$ for B-O. These results suggest that the MoS$_2$ QDs were successfully functionalized by APBA to form B-MoS$_2$ QDs.

The optical properties of B-MoS$_2$ QDs were investigated firstly by fluorescence spectrum. As shown in Fig. 3A, the fluorescence emission peak of B-MoS$_2$ QDs is at 375 nm, and the maximum excitation wavelength is at 300 nm in different wavelengths ranging from 280 nm to 315 nm. Comparing to MoS$_2$ QDs, the maximum excitation wavelength appears blue shift in B-MoS$_2$ QDs, because the amidation reaction occurs between MoS$_2$ QDs and APBA, which change the energy levels structure of MoS$_2$ QDs (Fig. 3B). Next, the UV-vis absorption spectrum and fluorescence spectrum of APBA, B-MoS$_2$ QDs, MoS$_2$ QDs, and APBA + MoS$_2$ QDs were studied for comparison. As illustrated in Fig. 3C for UV-vis absorption spectrum, the absorption peak of B-MoS$_2$ QDs locates at 340 nm, which is different from those of APBA (290 nm), MoS$_2$ QDs (320 nm), and APBA + MoS$_2$ QDs (275 nm). Meanwhile, the studies in fluorescence spectrum show that the fluorescence intensity of B-MoS$_2$ QDs is much stronger than those of MoS$_2$ QDs, APBA, and APBA + MoS$_2$ QDs (Fig. 3D). These results confirm further that the MoS$_2$ QDs is successfully modified with boronic acid groups, resulting the enhanced fluorescent response, and the B-MoS$_2$
QDs fluorescence emission is excitation-independent because the wavelength of maximum excitation without shift.\textsuperscript{42} Furthermore, the quantum yields of B-MoS\textsubscript{2} QDs is 46.5 \%, which is 30.0 times that of MoS\textsubscript{2} QDs (1.6 \%). Illustrated that the coupled effect between the MoS\textsubscript{2} QDs and boronic acid groups can result the improvement of QDs properties.

The stability and salt tolerance of B-MoS\textsubscript{2} QDs were also investigated and the corresponding results are shown in Fig. S2. It’s found that the fluorescence intensity of B-MoS\textsubscript{2} QDs remains unchanged under 302 nm UV light to exposure 80 min; and it is also stable in the presence of different concentration of NaCl, indicating that the synthesized B-MoS\textsubscript{2} QDs possesses excellent stability and salt tolerance, and it can be used as nanoprobe to construct fluorescence sensor.

\textit{Detection of o-DHB with B-MoS\textsubscript{2} QDs}

As we all know, it is a great challenge to distinguish selectivity o-DHB from its analogous, hence the fluorescent sensing of o-DHB was carried out based on the produced B-MoS\textsubscript{2} QDs as nanoprobe. Interestingly, we found that o-DHB can obviously quench the fluorescence of B-MoS\textsubscript{2} QDs, while the other analogous (m-DHB, p-DHB, ) show pretty weak fluorescence quenching of B-MoS\textsubscript{2} QDs (Fig. 4), suggesting that the analogous of o-DHB would not interfere the fluorescent detection of o-DHB and the B-MoS\textsubscript{2} QDs nanoprobe has high selectivity toward o-DHB.

To realize the best detection performance, the experiment conditions including pH value and reaction time were optimized (Fig. 5). It’s obtained the best fluorescence difference (F\textsubscript{0}-F) is presented at 8.0 of pH value, and the fluorescence intensity of B-MoS\textsubscript{2} QDs mixing with o-DHB reach to stay constant at 22 min. Therefore, these values (pH=8.0, incubation time= 22 min) were used as optimum conditions for the subsequent experiment.

Fig. 6 shows the fluorescence spectrum of the B-MoS\textsubscript{2} QDs at different concentrations of o-DHB (0.10 \(\mu\text{M} \sim 200.00 \mu\text{M}\)). It’s found that the fluorescence intensity decreases gradually with the
increase of o-DHB concentration, and there are two linear relationships between the o-DHB concentration and \((F-F_0)/F_0\) value: in the ranges from 0.10 μM to 10.00 μM, the linear equation is \((F-F_0)/F_0 = 0.02663C + 0.01576\) with a coefficient of 0.9939; in the ranges from 10.00 to 200.00 μM, the linear equation is \((F-F_0)/F_0 = 0.00267C + 0.2483\) with a coefficient of 0.9985. The limit of detection was calculated to be 0.02 μM (S/N = 3). To further evaluate the sensing performance of the B-MoS2 QDs nanoprobe, the comparisons between this work and the previous methods toward o-DHB were summarized in Table 1. Apparently, the proposed method in this work possesses more superior sensing performances (lower detection limit and wider linear range) than most of the previous works owing to the excellent advantages of B-MoS2 QD, implying that B-MoS2 QDs is an excellent fluorescence nanoprobe for o-DHB detection.

**Detection principle of o-DHB based on B-MoS2 QDs**

To explore the detection principle of o-DHB based on B-MoS2 QDs, the corresponding quenching mechanism of B-MoS2 QDs caused by o-DHB was studied through investigating the absorbance spectrum, fluorescence lifetime and fluorescence spectrum. From Fig. S3A, it’s noted that the absorbance spectrum of o-DHB overlapped with the excitation spectrum of B-MoS2 QDs, but not overlapped with the emission spectrum of B-MoS2 QDs, hence, the quenching mechanism was firstly considered to stem from IFE rather than fluorescence resonance energy transfer.\(^{43}\)

Next, in order to confirm the quenching mechanism belongs to either SQE or dynamic quenching effect (DQE), fluorescence quenching is described by the Stern-Volmer equation:

\[
[F_0-F]/F = K_{sv}[Q] = K_qτ_0[Q]
\]

Where \(F_0\) and \(F\) represent the fluorescence intensity of B-MoS2 QDs at \(λ_{em}=300\) nm in absence and presence of o-DHB, respectively; \(K_{sv}\) is the quenching constant; \([Q]\) is the concentration of o-DHB; \(K_q\) is the quenching rate constant; and \(τ_0\) represent fluorescence lifetime of B-MoS2 QDs (\(τ_0 =8.80\)
ns). As shown in Fig. 6B, the linear relationship is \((F-F_0)/F_0= 0.02663C + 0.01576 (R^2 =0.9939)\), which is suitable for the Stern–Volmer equation, and the quenching constant of Stern–Volmer \(K_{sv}(\lambda)=0.02663\). On the basic of the fluorescence lifetime of B-MoS\(_2\) QDs and \(K_{sv}\), \(K_q\) can be calculated to be \(3.03\times 10^{12}\) M\(^{-1}\)s\(^{-1}\), which is much higher than the maximum possible value for the dynamic effect \((1.0\times10^{10}\) M\(^{-1}\)s\(^{-1}\)). Considering the constant fluorescence lifetime and high quenching rate constant, the fluorescence quenching mechanism can be attributed to SQE. To conclude the results discussed above, IFE and SQE are considered to be the main mechanism for quenching the fluorescence of B-MoS\(_2\) QDs by o-DHB in this work.

**Selectivity and real application of B-MoS\(_2\) QDs for o-DHB**

The selectivity of B-MoS\(_2\) QDs for o-DHB was investigated by addition of possible interferences including ions (Ca\(^{2+}\), Cu\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), Cl\(^{-}\), K\(^{+}\)), typical phenols (m-DHB, p-DHB, bisphenol A, phenol, nitrophenol) . As demonstrated in Fig. S4, the B-MoS\(_2\) QDs fluorescence intensity has little changes in the presence of interferes with high concentration, suggesting the B-MoS\(_2\) QDs nanoprobe has excellent selectivity for o-DHB detection.

In order to research the application of B-MoS\(_2\) QDs for sensing o-DHB in real water sample, two kinds of water sample (tap water and lake water ) were introduced in this procedure. Certain amounts of o-DHB were spiked in the introduced water samples. After dilution with 0.1 M PBS (pH 8.0), the concentration of o-DHB in each sample was measured by B-MoS\(_2\) QDs and the corresponding results were shown in Table S1. From Table S1, it can be noted that the recoveries are 93.35-108.8% and the relative standard deviations are lower than 3.50%, indicating that this method has high accuracy and great potential for o-DHB detection in real water.

**Conclusion**
In summary, B-MoS$_2$ QDs with excellent fluorescence, salt tolerance and stable properties was synthesized and used as fluorescence sensing nanoprobe for detecting o-DHB. The B-MoS$_2$ QDs can not only show excellent selectivity toward o-DHB owing to the reaction between the ortho-diol structure of B-MoS$_2$ QDs and o-DHB, which can detect successfully o-DHB from its analogues and other interferes, but also it can show low detection limit (0.02 μM) and wide linear range (0.10-200.00 μM). The studies in detection mechanism demonstrated that the fluorescence quenching of B-MoS$_2$ QDs by o-DHB is ascribed to the IFE and SQE. Furthermore, the produced B-MoS$_2$ QDs nanoprobe was successfully applied in real water samples for o-DHB analysis. It’s confirmed that this work has promising applications in fluorescence sensing of o-DHB.

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Scheme 1. Schematic illustration for synthesizing B-MoS₂ QDs and its application as fluorescence nanoprobe for o-DHB detection.
Fig. 1 TEM images of MoS$_2$ QDs (A) and B-MoS$_2$ QDs (B), inset: size distribution of MoS$_2$ QDs and B-MoS$_2$ QDs.
Fig. 2 XPS survey spectra of B-MoS₂QDs (red) and MoS₂QDs (black) (A); High-resolution peak-fitting XPS spectra of the B 1s (B), Mo 3d (C) and S 1s (D).
Fig. 3 Fluorescence emission spectra of B-MoS$_2$ QDs under different excitation wavelengths (A).

Fluorescence emission spectrum of MoS$_2$ QDs (red curve) and B-MoS$_2$ QDs (blue curve) (B).

UV-vis absorption spectra (C) and fluorescence spectra (D) of APBA (0.1 M), APBA+ MoS$_2$ QDs, B-MoS$_2$ QDs and MoS$_2$ QDs; (the concentration of B-MoS$_2$ QDs and MoS$_2$ QDs were 0.1 μM).
Fig. 4 Fluorescence spectrum of the B-MoS$_2$ QDs solution with various phenols (The concentration of m-, p- and o- DHB are 1.00 mM, 1.00 mM and 100.00 μM).
Fig. 5 Fluorescence spectrum responses of the B-MoS₂ QDs with 150.00 μM o-DHB at different pH value (A); fluorescence intensity responses of the B-MoS₂ QDs with 150.00 μM o-DHB at different pH value (the black histograms is the fluorescence intensity of the B-MoS₂ QDs, the red histograms is the fluorescence intensity of B-MoS₂ QDs + o-DHB.) (B); fluorescence spectrum responses of of the B-MoS₂ QDs with 150.00 μM o-DHB incubate different time (C); fluorescence intensity responses to the different time (D). The error bars were calculated from the results of three independent experiments.
Fig. 6 Fluorescence spectra of B-MoS$_2$ QDs upon the addition of different concentration of o-DHB in the range of 0.10–10.00 μM and 10.00- 200.00 μM (A); the plot of fluorescence intensity ratios of (F$_0$-F)/F$_0$ at 375 nm versus the concentration of o-DHB (B), inset: relationship and linear fitting between the fluorescence intensity of the B-MoS$_2$ QDs and the concentrations of added o-DHB (0.10 μM–10.00 μM).
Table 1 Comparison of the determination for o-DHB using different methods.

| Nanoprobe          | Detection method | Linear range (μM) | Detection Limit (μM) | Reference |
|--------------------|------------------|-------------------|---------------------|-----------|
| NCDs               | Fluorimetry      | 2.70-344.00       | 0.30                | 44        |
| CPBA-CDs           | Fluorimetry      | 0.10-56.00        | 0.10                | 45        |
| Au-PdNF/RGO/GCE<sup>a</sup> | Electrochemical  | 2.50-500.00       | 0.80                | 46        |
| AuNCs              | Fluorimetry      | 0.10-10.00        | 0.06                | 47        |
| np-GE<sup>b</sup>  | Electrochemical  | 50.00-1000.00     | 1.78                | 48        |
| Si NPs             | Fluorimetry      | 0.10-40.00        | 0.02                | 49        |
| PANI nanorods<sup>c</sup> | Electrochemical | 5.00-100000.00    | 2.10                | 50        |
| DCIL<sup>d</sup>   | Fluorimetry      | 1.00-1000.00      | 0.40                | 51        |
| CS-NIP BDD<sup>e</sup> | Electrochemical | 0.80.00           | 0.69                | 52        |
| B-MoS<sub>2</sub> QDs | Fluorimetry      | 0.10-200.00       | 0.02                | This work |

<sup>a</sup> Au-PdNF/RGO/GCE, Au-Pd nanoflower/reduced graphene oxide modified glassy carbon electrode;
<sup>b</sup> np-GE, nanoporous gold electrode;
<sup>c</sup> PANI nanorods, porous polyaniline nanorods;
<sup>d</sup> DCIL, dicaticionic ionic liquid;
<sup>e</sup> CS-NIP BDD, chitosan (CS) film electrodeposited on boron doped diamond.