Electronic Supplementary Information

A novel photoluminescence sensing system sensitive for and selective to bromate anions based on carbon dots

Ping Li,[ac] Xiang-Ying Sun,*[b] Jiang-Shan Shen [b] and Bin Liu [b]

[a]College of Chemical Engineering, Huaqiao University, Xiamen, 361021, China

[b]College of Materials Science and Engineering, Huaqiao University, Xiamen, 361021, China

[c]Department of Chemistry, Ningde Normal University, Ningde, 352100, China

*Correspondence to sunxy@hqu.edu.cn, liumy@hqu.edu.cn (S. Xiangying), Tel:+86-592-6162231, Fax: +86-592-6160088.

Table of contents in Electronic Supplementary Information:

1 Synthesis of the CDs

0.5 g PEI and 1.0 g CA were mixed. Then, the mixed solid was dissolved by 10 mL hot water in a 25 mL beaker. The resulting solution was heated to 180 °C by an oil bath. After 20 min, most of water were evaporated, and a uniform pale-yellow gel formed. In order to avoid that the gel was scorched, 10 mL water were successively added into the beaker by dropwise and 180 °C was kept. The procedure of adding water was repeated for 10 times within 3 h [30]. The color of the gel gradually turned into deep yellow, and eventually became orange, which was indicative of the formation of the CDs @ PEI.

2 QY measurements

Reference on QY measurements: Lakowicz, J.R. Principles of Fluorescence Spectroscopy, 2nd Ed., 1999, Kluwer Academic/Plenum Publishers, New York. The QY of the CDs @ PEI was measured with quinine sulfate as a reference (QY = 0.54 in 0.1 M H_2SO_4, excited at 360 nm). QY was calculated according to the following equation:

$$\mathrm{QY} = QY_R \frac{I\, OD_R n^2}{I_R\, OD\, n_R^2}$$

Where QY is the quantum yield, I is the measured integrated emission intensity, n is the refractive index, and OD is the optical density. The subscript R refers to the reference fluorophore of known QY (quinine sulfate used in the work). In order to minimize re-absorption effects, absorbance in the 1 cm fluorescence cuvette were kept under 0.05 at the excitation wavelength.

3 Figure S1: FT-IR spectra of the CDs and CDs @ PEI

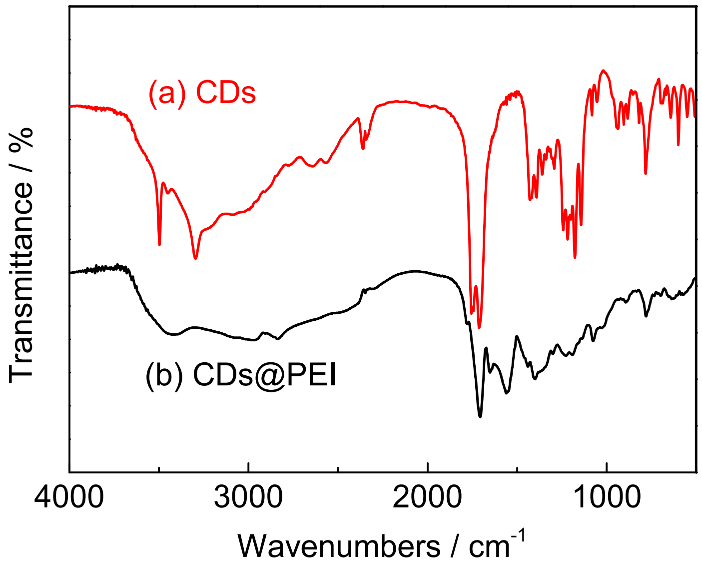

Fig.S1. FT-IR spectra of the CDs and CDs@PEI prepared by employing CA as the carbon source in the absence (a) and in the presence (b) of PEI as the passivation agent.

4 Figure S2: The change of PL emission spectra of the CDs@PEI with different excitation wavelength

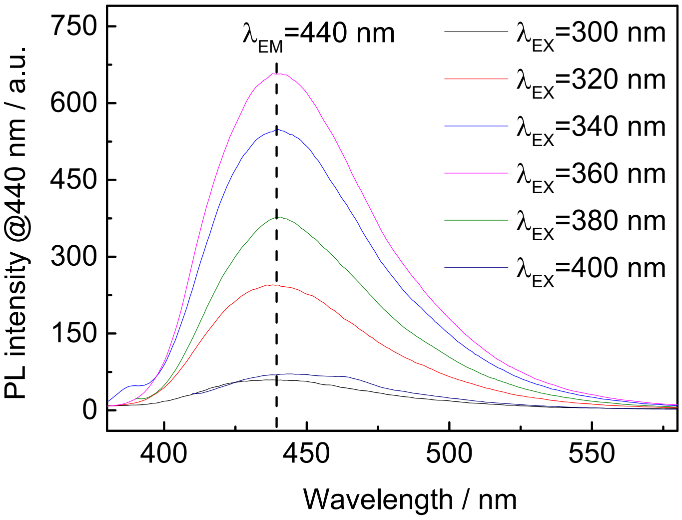

Fig.S2. The PL emission spectra of CDs@PEI under different excitation wavelength with 20 nm increments from 300 to 400 nm. The concentration of CDs@PEI was 6.0 μg mL^{-1}.

5 Figure S3-S4: PL stability of the CDs @ PEI

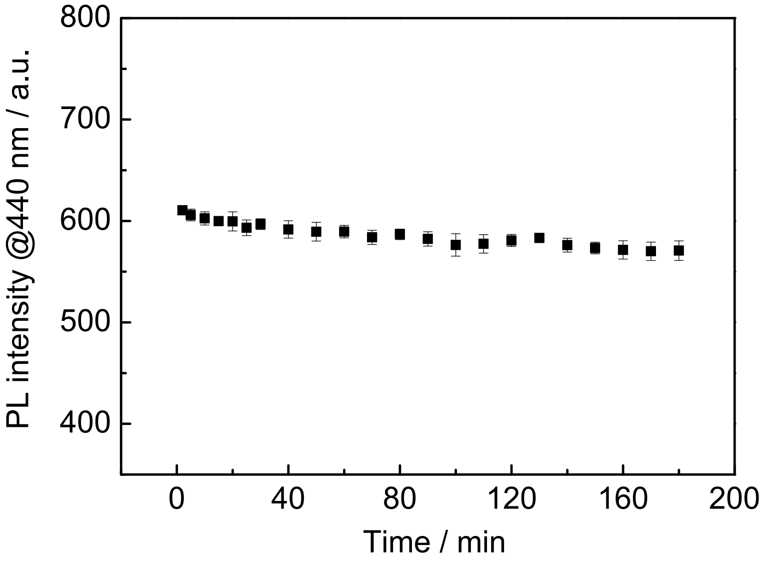

Fig.S3. The change of PL intensity @440 nm of CDs@PEI with various irradiation time under 365 nm UV lamp, and 3100 lux of light intensity. The concentration of CDs@PEI was 6.0 μg mL^{-1}.

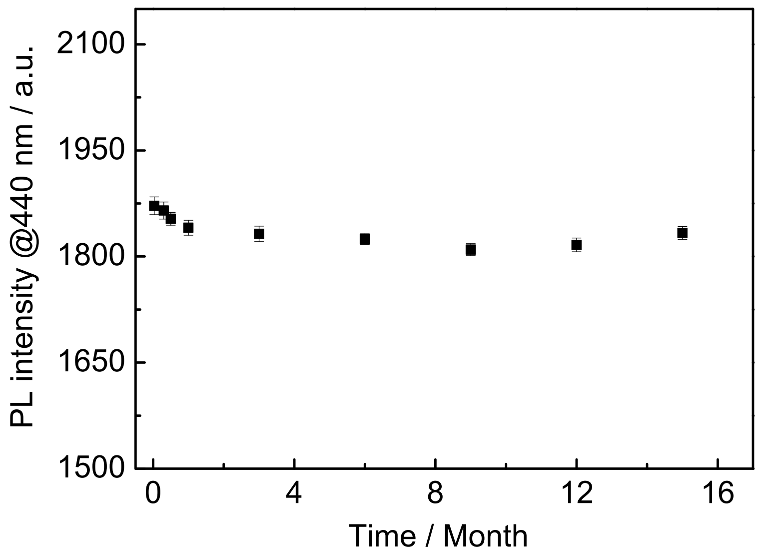

Fig.S4. The change of PL intensity @440 nm of CDs@PEI with various storage time. The concentration of CDs@PEI was 18 μg mL^{-1}.

6 Figure S5: The relationship curve between $\Delta F/F_0$ and HCl concentration

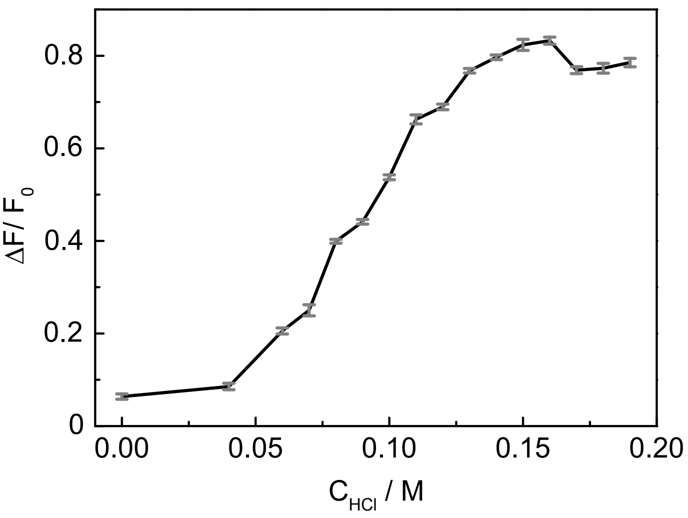

Fig.S5. The concentrations of CDs@PEI, KBr and BrO_3^- anions were 6.0 μg mL^{-1}, 0.46 mM and 0.60 μM, respectively. Interaction time was 2.5 h. The error bars were obtained from the standard deviation of three parallel measurements.

7 Figure S6: The relationship curve between $\Delta F/F_0$ and KBr concentration

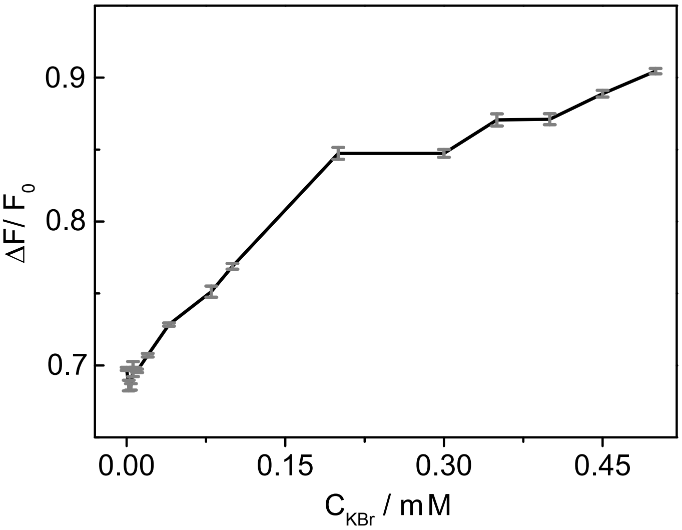

Fig.S6. The concentrations of CDs@PEI, HCl and BrO_3^- anions were 6.0 μg mL^{-1}, 0.12 M and 0.60 μM, respectively. Interaction time was 2.5 h. The error bars were obtained from the standard deviation of three parallel measurements.

8 Figure S7: The relationship curves between interaction time and PL intensity

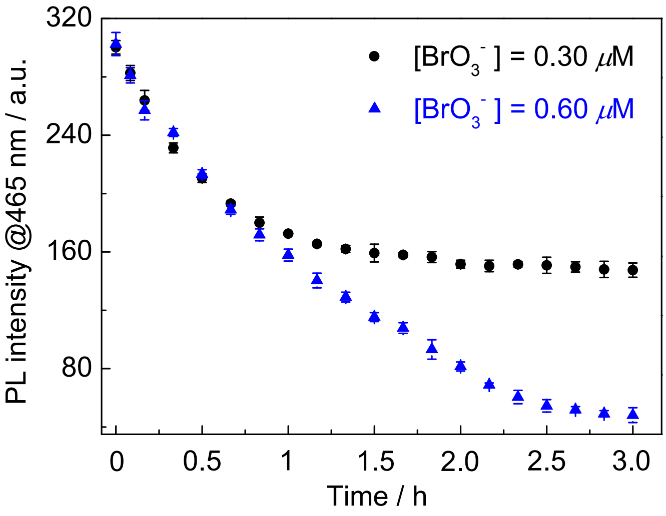

Fig.S7. The relationship curves between interaction time and PL intensity @465 nm under 0.30 μM (●) and 0.60 μM (▲) BrO_3^- anions, respectively. The concentrations of CDs@PEI, HCl and KBr were 6.0 μg mL^{-1}, 0.12 M, and 0.46 mM, respectively. The error bars were obtained from the standard deviation of three parallel measurements.

9 Figure S8: The reproducibility of the CDs@PEI obtained from

different batch of sensing BrO$_3^-$ anions

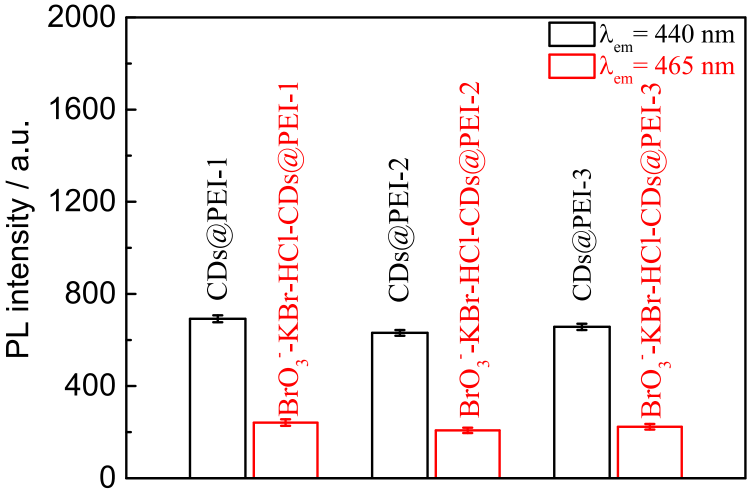

Fig.S8. The comparison of PL intensity at maximum emission wavelength of CQDs@PEI prepared by three batches in the absence (black bar) and in the presence (red bar) of BrO$_3^-$-KBr-HCl solution. The concentrations of CDs@PEI, HCl, KBr and BrO$_3^-$ anions were 6.0 μg mL^{-1}, 0.12 M, 0.46 mM and 0.20 μM, respectively. Interaction time was 1 h. The error bars were obtained from the standard deviation of three parallel measurements.

10 Figure S9: The change of PL intensity of the sensing system with increasing KBr and BrO$_3^-$ anions

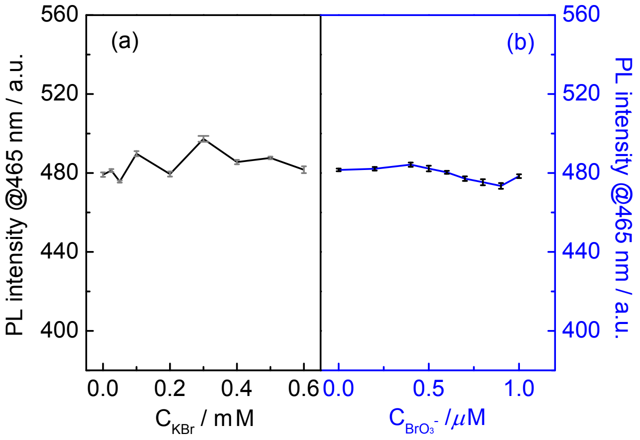

Fig.S9. The change of PL intensity @465 nm of this sensing system with increasing KBr (a) and BrO_3^- anions (b). CDs@PEI and HCl concentrations were 6.0 μg mL^{-1} and 0.12 M, respectively. Interaction time was 2.5 h. The error bars were obtained from the standard deviation of three parallel measurements.

11 The related calculation of thermodynamic

According to the half-reaction of electrode pair of Eq.1 and its standard electrode potential,

$$\text{Eq.1} \quad Br_2 + 2e \leftrightarrow 2\,Br^-, \qquad \varphi^{\theta}{}_{\left(Br_2/Br^-\right)} = 1.08\ \text{V}$$

The electrode potential of $\varphi_{\left(Br_2/Br^-\right)}$ under experimental conditions could be calculated, according to the Nernst equation (formulae. 1),

$$\varphi_{\left(Br_2/Br^-\right)} = 1.08 + (0.059/2) \times lg\left([Br_2]/[Br^-]^2\right)$$

$$= 1.08 + (0.059/2) \times lg\left(1/[4.6 \times 10^{-4}]^2\right)$$

$$= 1.28\,V$$

Furthermore, the half-reaction of electrode pair of Eq.2 and its standard electrode potential,

Eq.2 $BrO_3^- + 6H^+ + 5e \leftrightarrow 1/2\ Br_2 + 3H_2O$, $\varphi^{\theta}_{\left(BrO_3^-/Br_2\right)} = 1.52\ V$

According to the Nernst equation, the electrode potential of $\varphi_{\left(BrO_3^-/Br_2\right)}$ under experimental conditions could be calculated,

$$\varphi_{\left(BrO_3^-/Br_2\right)} = 1.52 + (0.059/5) \times lg\left(\left[BrO_3^-\right]\left[H^+\right]^6/[Br_2]^{1/2}\right)$$

$$= 1.52 + (0.059/5) \times\ lg\left(0.6 \times 10^{-6} \times 0.12^6/1\right)$$

$$= 1.51\ V$$

Therefore, the difference of two electrode potentials $\Delta\varphi$ could be calculated to be 0.23 V.

According to the equation of $\Delta G = -n\Delta\varphi F$,

$$\Delta G = -22.20\ kJ\ mol^{-1} < 0$$

Therefore, the following reaction should occur, which will generate active Br_3^- anions.

$$Br_2 + Br^- \rightarrow Br_3^-$$