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COMMUNICATION

Polyamine-functionalized carbon nanodots: a novel chemiluminescence probe for selective detection of iron (III) ionsLixia Zhao^{1,a,*}, Fanglan Geng^{1,a}, Fan Di^a, Liang-Hong Guo^{*,a}, Bin Wan^a, Yu Yang^a, Hui Zhang^a and Guozhu Sun^b

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We firstly studied the chemiluminescence behavior of branched poly(ethylenimine)-functionalized carbon dots (BPEI-CDs). The results demonstrated that BPEI-CDs can be as a novel chemiluminescence probe in alkaline solution for rapid detection of iron(III) ions with high sensitivity and selectivity. Possible CL mechanism was studied by UV-Vis, fluorescence, CL, FTIR, XPS and EPR spectroscopy. Iron (III) can be selectively captured by the surface functional groups of BPEI and injected holes into carbon dots which resulted in great improvement of BPEI-CDs CL signal in alkaline solution. The work sheds new light on the characteristics and further application of functionalized carbon dots.

Carbon nanodots (CDs), as a newcomer to the world of nanomaterials, have attracted intensive attention due to their alluring luminescence properties and wide application in many areas of fundamental and technical importance. Luminescent properties of carbon dots were usually investigated by photoluminescence (PL) produced using photoexcitation,¹⁻⁷ and electrochemiluminescence (ECL) generated by electron injection.⁸⁻¹¹ Chemiluminescence (CL) known as the emission of light from chemical reactions has proved to be a useful phenomenon due to its ever increasing analytical application for its high sensitivity and lack of background scattering light interference. Therefore, the CL behavior of CDs with its related analytical application has been increasing paid attention recently.

To date, the CL behavior of carbon dots has been investigated by many groups when it coexisted with oxidants (KMnO₄, Ce(IV), NaIO₄, NaClO, KFe(CN)₃)¹²⁻¹⁶ or ultraweak CL system (H₂O₂-NaHSO₃, H₂O₂-HNO₂ or Co²⁺-H₂O₂)¹⁷⁻¹⁹ or CL reagents such as luminol²⁰. However, These system mainly focused on the CL behavior and mechanism of CDs. For the analytical application of CDs based on their CL, there are limited report. To the best of our knowledge, only CDs-oxidants (NaClO¹⁶, KFe(CN)₃)¹⁴ CL system and CDs-ultraweak CL system (H₂O₂-HNO₂¹⁷ or Co²⁺-H₂O₂¹⁹) for the detection of reducing substances such as dopamine, nitrites, chlorine, and cobalt ions were reported. Intense research still focused on exploring the new CDs-based CL systems and obtaining new insight into the CDs CL characteristics and its further application.

Recently, we found the CL behavior of CDs in the alkaline solution without the presence of any CL reagent or CL system or

oxidants²¹. The CL system had very good reproducibility. But when it was used for the analytical application, there were two bottlenecks: firstly, the CL intensity was very small due to the low quantum yield of CDs (only 10%)⁸; secondly, the selectivity was very poor. While Branched polyamine-functionalized CDs (BPEI-CDs) not only exhibit the excellent optical properties (42.5% FL quantum yield), but also are envisioned to be applicable in chemical sensing because the polyamine has a broad complexing property for transition metal ions^{22,23}. Based on these, the CL properties of BPEI-CDs in alkaline solutions was firstly studied. Similar to the unmodified CDs²¹, BPEI-CDs can generate CL signal in strong alkaline solutions and the CL intensity was higher than the unmodified CDs. Moreover, the effects of various coexisting ions in water samples on the CL signal were investigated. Interestingly, only iron (III) improved the CL intensity of BPEI-CDs in the alkaline solution. This suggested that BPEI-CDs can be a novel chemiluminescence probe for the rapid detection of trace ferric ions in water samples with high selectivity and sensitivity which is proved to be difficult in the past²⁴.

To perform the experiments, polyamine-functionalized carbon dots (BPEI-CDs) were synthesized by the low temperature pyrolysis using citric acid (CA) as carbon source due to its low carbonization temperature (<200°C) and branched poly(ethylenimine) (BPEI) as functional reagent according to the manuscript²⁵ with some modification. X-ray photoelectron spectroscopy (XPS) (Fig.S1(ESI†)) showed that the as prepared BPEI-CDs contain carbon, nitrogen and oxygen, the characteristic peak of C-C sp² appearing suggested that abundant graphite structures formed (C 1s spectrum). Fourier transform infrared (FTIR) spectroscopy (Fig.S2(ESI†)) showed that there were many characteristic absorption bands of BPEI and amide, but nearly no absorption of CA, which indicated that the CA was mostly carbonized, BPEI was kept stable and coated at the surface of CDs by the amide linkaged as previously reported. High resolution transmission electron microscopy (HRTEM) results suggested that the BPEI-CDs were mostly spherical morphology with an average diameter of 3.5-4.5 nm and lattice spacing of 0.31 nm which matches the <002> spacing of graphitic carbon (Fig.S3 (ESI†)).

As the other carbon dots characters, The photoluminescence (PL) emission of BPEI-CDs shifted as the excitation wavelength increased with the centered PL wavelength of 450 nm (Fig.S4

(ESI[†]). UV-vis absorption bands results showed that the BPEI-CDs have two absorption spectra centered at 245 nm and 353 nm (Fig S5(ESI[†])). However, the addition of Fe(III) into the BPEI-CDs solution gave rise to a new broad band found in the range from 270 nm to 330 nm, while the absorption bands centered at 245 nm of BPEI-CDs and the absorption bands at 224 nm of Fe(III) diminished even disappeared. The same changes of the absorption spectrum were also observed when Fe(III) ions were added into BPEI. This indicated a complex reaction happened between BPEI capped on the surface CDs and Fe(III) ions.

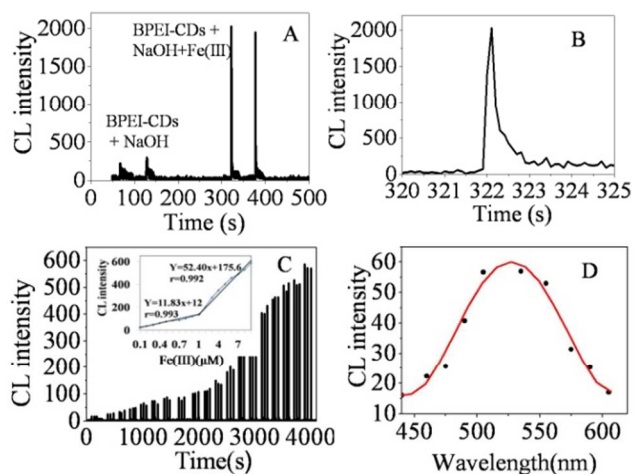


Fig. 1 (A) Improvement of the CL intensity with Fe(III) ions added into the BPEI-CDs-NaOH CL system. (B) CL kinetic curve of BPEI-CDs-NaOH-Fe(III) system (C) CL signals in the presence of different concentrations of Fe(III) ions. Inset: the calibration curve for Fe(III) ions. (D) CL spectrum of BPEI-CDs-NaOH-Fe(III) ions system. The concentrations of carbon dots, NaOH and Fe(III) ions are 7.5 mg/ml, 0.1 M and 1 mM, respectively.

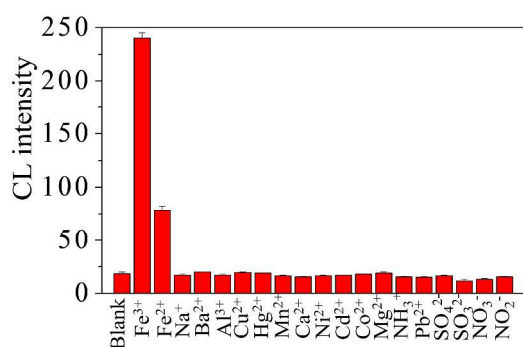


Fig. 2 Selectivity of the BPEI-CDs-based CL sensing for Fe(III) ions in alkaline solution. The concentrations of carbon dots, NaOH and Fe(III) are 7.5 mg/ml, 0.1 M and 1 μM, respectively, the concentrations of other common ions in water were all 10 μM.

We then tested whether the BPEI-CDs could act as a chemiluminescence probe for Fe(III) ions in alkaline solutions. As demonstrated in Fig.1A, the BPEI-CDs exhibited weak chemiluminescence only in NaOH solution. While in the presence of Fe(III) ions, the chemiluminescence signal increased drastically and reached the maximum within 1.5 s (Fig.1B). Moreover, with the increase of Fe(III) concentration, the CL intensity improved linearly (Fig.1C). The CL intensity was also dependent on the concentration of NaOH and carbon dots in a

certain range Fig. S6 (ESI[†]). In order to obtain a low detection limit and a good recovering condition, 0.1 M NaOH and 7.5 mg/ml BPEI-CDs were selected.

Based on these, the capability of BPEI-CDs as a chemiluminescence probe for quantitative detection of Fe(III) was evaluated. As shown in Fig.1C, there are two linear regions between CL intensity and Fe(III) concentration, one from 1×10^{-7} M to 1×10^{-6} M with a correlation coefficient of 0.993, and the other from 1×10^{-6} M to 1×10^{-5} M with a correlation coefficient of 0.992. The relative standard deviation (RSD) ($n=9$) of the analysis were 2.3%, 3.0%, 1.9% for Fe(III) concentration of 5.0×10^{-7} M, 1.0×10^{-6} M and 5.0×10^{-6} M, respectively. The limit of detection ($S/N=3$) for Fe(III) was 6.67×10^{-8} M which is far lower than the WHO guideline recommendation of 0.3 mg/L-3.0 mg/L in drinking water.

The selectivity of the sensing method for Fe(III) ions was evaluated before its application in the real water samples. The influence of various environmentally relevant coexisting ions in water on the CL was tested (Fig.2). It could be seen that only Fe(III) ions effectively improved the chemiluminescence signal of BPEI-CDs in NaOH solution, whereas no obvious CL signal changes were observed for other relevant ions. These results demonstrated that the BPEI-CDs can be a CL probe for the highly selective toward Fe(III) ions over other relevant ions.

The excellent specificity combined with high sensitivity and fast response of BPEI-CDs to Fe(III) ions suggested that our method might be directly applied to the detection of Fe(III) ions in real samples. Therefore, we further examined the practicality of the assay by testing Fe(III) ions in natural water (tap water and river water). The results were shown in table S1(ESI[†]). It can be seen that the recoveries for three samples were satisfactory, thus further demonstrating the applicability of the proposed methodology.

The chemiluminescence characteristics of the BPEI-CDs was investigated, CL spectrum of BPEI-CDs-NaOH-Fe(III) system was measured by a fluorescence spectrometer using high-energy cutoff filters of various wavelengths and compared with the PL spectrum. As shown in Fig 1D, the maximum CL spectrum were located in the wide range of 430-600 nm with centered at 530 nm. The wide range was similar to the fluorescence emission spectrum of the BPEI-CDs. Hence, it was reasonable that CL could be attributed to the various surface energy traps that existed on the BPEI-CDs. The CL peak was red-shifted in comparison to the most intense PL peak (centered at 450 nm), which mainly occurred through excitation and emission within the core of the nanoparticles. The red-shift most likely resulted from the smaller energy separations of the BPEI-CDs surface states compared with the energy for the most intense PL²⁶. Furthermore, superoxide dismutase (SOD), thiourea and histidine, the quencher of superoxide ion, hydroxyl free ion and singlet oxygen, had no inhibition on the CL signal of the system. De-oxygenated solutions also had no inhibitory effect on the CL, which indicated that the dissolved oxygen had little effect on the CL and the singlet oxygen emitter could be excluded in the BPEI-CDs-NaOH-Fe(III) system.

EPR was utilized to investigate the ground-state properties of luminescent species in the BPEI-CDs. The carbon dots showed EPR signal at $g = 2.0022 \pm 0.000076$ (ESI[†]), which revealed a

singly occupied orbital in ground-state BPEI-CDs. The singly occupied orbital indicated that BPEI-CDs could be electron donors or acceptors during the reaction. EPR spectra of the BPEI-CDs in NaOH and NaOH-Fe(III) system were also presented in Fig. S7(ESI[†]). The g value of the BPEI-CDs increased from 2.0022 ± 0.000029 to 2.0031 ± 0.000050 in a NaOH solution, so electron transfer was suggested after the “the chemical reduction” reaction, similarly to the hydroxyl-CDs²¹. With the addition of Fe(III), the g value was reduced from 2.0031 to 2.0027 which suggested that Fe(III) in basic solutions can as oxidant to inject the holes into the BPEI-CDs through oxidation like KMnO_4 ¹².

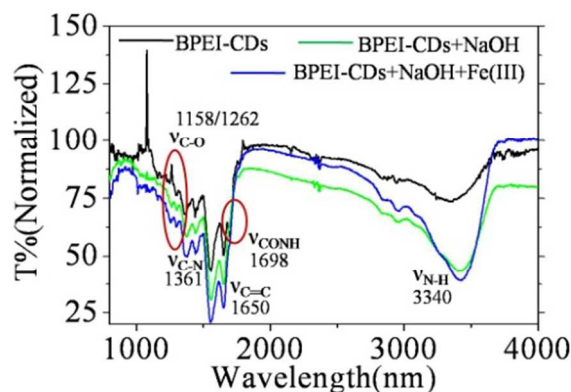


Fig. 3 FTIR spectrum of pristine BPEI functionalized carbon dots (black line), NaOH-treated BPEI-CDs (green line) and BPEI-CDs after reaction with NaOH and Fe(III) (blue line)

In order to verify the CL mechanism, the pristine BPEI-CDs, NaOH-treated BPEI-CDs and Fe(III)-NaOH treated BPEI-CDs were characterized through fourier transform infrared spectroscopy (FTIR)(Fig.3). The results revealed that many functional groups such as, -C-H-, C-N, -CONH-(amide), N-H, were detected on the BPEI-CDs, in agreement with previous studies. For NaOH-treated BPEI-CDs, there showed a significant reduction in the amount of carbon-oxygen double bonds in amide at 1698 cm^{-1} and the appearance of carbon-oxygen single bond at 1158 cm^{-1} , which indicated that the surface carbon-oxygen double bonds in amide were probably partly reduced to carbon-oxygen single bond. With the addition of Fe(III), the surface functional groups did not change. While from the X-ray photoelectron spectroscopy (XPS) spectrum of Fe(1s) (Fig.S8(ESI[†])), the Fe^{2+} and Fe^0 peak around 709.9 eV and 711.2 eV appeared (Fe 2p) after the CL reaction which indicated that the Fe(III) acted as the oxidant in the CL reaction.

Based on the above study, a possible CL mechanism for BPEI-CDs-NaOH- Fe(III) system is proposed and illustrated as shown in Fig.4. The single orbital of BPEI-CDs detected by EPR spectra could serve as the electron or hole traps. In the presence of NaOH, the injected electrons through “chemical reduction” annihilate with thermally excited generated holes to produce the weak CL signal. Fe(III), which can be captured by the surface functional groups of BPEI, could inject holes into the BPEI-CDs as the oxidant. The holes injection through the oxidation reaction accelerated the electron-hole annihilation, which resulted in a higher CL intensity.

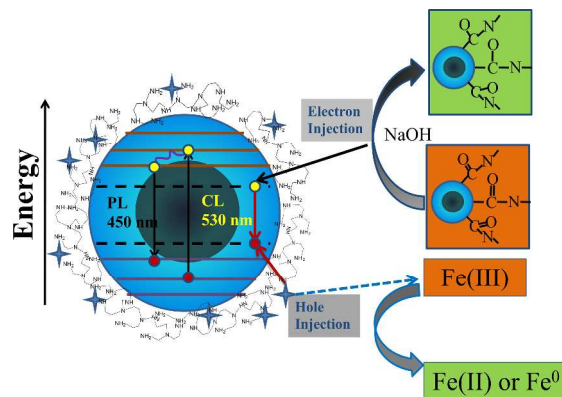


Fig. 4 Schematic illustration of possible FL and CL mechanism of BPEI-CDs-NaOH-Fe(III) system

In conclusion, polyamine-functionalized CDs were found to act as the chemiluminescence probes for Fe(III) detection with high selectivity and sensitivity in water solution. The method relied on the facts that BPEI-CDs can generate CL signal in the alkaline solution, and Fe(III) ions captured on the surface of the BPEI-CDs can act as an oxidant to inject holes into the BPEI-CDs and result in great improvement of BPEI-CDs CL signal. The assay platform has two important features: Firstly, the method provides a convenient “mix-and-detect” procedure for homogeneous and rapid detection of Fe(III). Additionally, this assay exhibits high sensitivity and selectivity toward Fe(III) versus other metal ions, wide linear range and low cost. It has been demonstrated to have promising applications in the detection of Fe(III) in environmental water samples. It is evident from the present work that functionalized CDs can also generate chemiluminescence in strong alkaline solution, and trace levels of certain metal ions could be rapidly and selectively detected by using appropriate surface functionalized CDs as the chemiluminescence probe, suggesting promising analytical applications of CDs.

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