Electrochemiluminescence Quenching Sensor of a Carboxylic Carbon Nanotubes Modified Glassy Carbon Electrode for Detecting Crystal Violet Based on Nitrogen-doped Graphene Quantum Dots@Peroxydisulfate System

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In this work, the electrochemiluminescence system of nitrogen-doped graphene quantum dots (N-GQDs) and K₂S₂O₈ was built for the determination of crystal violet (CV). Meanwhile, a carboxylic carbon nanotubes modified glassy carbon electrode (CCNTs/GCE) was used as an ECL sensor. Thanks to the excellent electron transfer ability and large surface area of CCNTs, the ECL signal of N-GQDs@S₂O₈²⁻ was remarkably amplified. With the presence of a low concentration of CV, a distinct decrease of the ECL signal was observed due to a quenching effect of CV on the ECL emission. Moreover, the quenched ECL intensity responded linearly to the logarithm of CV concentration within the range of 0.05 – 5 μmol/L, with a LOD of 45 nmol/L (S/N = 3). The proposed ECL system exhibited high sensitivity and specificity to CV, which was successfully applied in the practical detection of CV in real water samples from a local fishpond farm.

Keywords Electrochemiluminescence, quenching sensor, crystal violet, nitrogen-doped graphene quantum dots, carboxylic carbon nanotubes

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Introduction

Crystal Violet (CV) is a well-known synthetic colorant which is extensively utilized in the textile industry and as a biological stain.¹ Due to its high-effective effects of anti-microbial, anti-parasitic, and anti-fungal properties, CV has been widely used for the treatment and prevention of certain fish diseases in the aquaculture filed.² As a cationic triphenylmethane dye, CV has mutagenic and carcinogenic effects on aquatic biota and humans. So far, various methods have been developed for CV determination, including spectrophotometer,³ high-performance liquid chromatography,⁴ chemometric-assisted method,⁵ etc. However, these methods are expensive, complicated operation, and time-consuming. As a new developing analytical tool, electrochemiluminescence (ECL) that combines the chemiluminescence and electrochemistry possesses the advantages of high sensitivity, temporal and spatial control, low cost, fast response, and good reproducibility.⁶,⁷ Based on the enhancing or quenching effect on the ECL systems, many target analytes, e.g. various metal ions,⁸ organic pollutants,⁹-¹¹ food additives,¹²,¹³ and proteins,¹⁴,¹⁵ had successfully been detected. The ECL system generally consists of ECL luminophores and coreactants. Apart from the conventional ECL luminophores (such as ruthenium complexes, luminol, and luminol derivatives), the new group of ECL luminophores, quantum dots (QDs) with different sizes, shapes, and chemical components, have recently gained increasing attention,¹⁹-²² since they exhibit more stable ECL and sensitivity. However, the metal-based QDs are toxic and poorly soluble, which limit their application in sensing field. Graphene QDs (GQDs) are considered as an ideal alternative for ECL sensors fabrication, due to their obvious advantages of low toxicity, facile synthesis, excellent chemical inertness.²³-²⁵ Coreactants, e.g. hydrogen peroxide and peroxydisulfate, dominantly contributes to the whole ECL process, owing to the ECL behaviors of GQDs mostly follow the coreactant pathway.²⁶,²⁷ The ECL system of GQD@H₂O₂ had been used for the ultrasensitive detection of adenosine triphosphate.²⁸ Compared to GQDs, N-GQDs showed considerably stronger fluorescence emission.²⁹ Doping with heteroatoms can offer more active sites and effectively tune their optical property, which would expand GQDs-based sensing applications.³⁰,³¹

In order to obtain an intense ECL signal and ideal analytical performance, many materials, such as metal nanoparticles or carbon nanotubes (CNTs), had been used for ECL signal amplifying.³²-³⁴ The ECL intensity of CNTs/ZnO nanocomposites was almost an order of magnitude greater than that of pure ZnO nanoflowers, owing to the CNTs decreased the barriers to ZnO reduction during the ECL process.³⁵

In the present work, the ECL system of N-GQDs@K₂S₂O₈ was built for the determination of CV. And the CCNTs were modified onto the GCE in order to amplify the ECL signal and to obtain the analytical sensitivity. The proposed ECL system for CV showed a linear relationship between the CV concentration and the ECL intensity.
concentration with an ECL intensity decrease over the range from 0.05 - 5 μmol/L ($r = 0.9905$). The detection limit was obtained as 45 nmol/L. In addition, the proposed method exhibited its potential application for the practical detection of CV in fishpond water.

**Experimental**

**Reagents and chemicals**

CV was purchased from Shanghai Yuanye Bio-Technology Co., Ltd., cupric chloride dihydrate, citric acid monohydrate, and potassium persulfate were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Phosphate-buffered saline (PBS) solutions with various pH values were prepared by stock solution of 0.1 mol/L KH$_2$PO$_4$ and K$_2$HPO$_4$. All other chemicals were of analytical grade and used without further purification. The solutions were prepared by using doubly distilled water.

The CCNTs were prepared as follows: 0.2 g CNTs were added into 100 mL 3:1 (v/v) H$_2$SO$_4$:HNO$_3$, then refluxed at 120°C for 1 h, the solution was finally filtered using a 0.8-μm membrane. The residue was washed by water until pH = 7 and dried in an oven at 60°C for 8 h to obtain the CCNTs.

The N-GQDs were prepared as follows: 8.0 g citric acid monohydrate and 1.0 mL ammonia were added into an autoclave and heated at 210°C for 1.5 h, and then cooled to room temperature naturally. After cooling to room temperature, the N-GQDs solution was mixed with excess ethanol, allowed to stay there for 15 min, and then centrifuged at 13000 rpm for 5 min to remove any impurities. After purification, the resultant N-GQDs was diluted to 50 mL with water for further use.

**Apparatus**

Cyclic voltammetry and ECL experiments were performed using an MPI-B ECL analyzer system (Remax Analysis Instruments Co., Ltd., Xi’an, China). A conventional three-electrode system was set up for ECL experiments, consisting of a modified GCE (3 mm in diameter) as the working electrode, a platinum foil as the auxiliary electrode, and a saturated calomel electrode as the reference electrode, respectively.

Scanning electron microscope (SEM) was carried out with a JSM-6360LA SEM instrument. A detachable glassy carbon electrode was employed for morphology observation of CCNTs/GCE. Electrochemical impedance analysis (EIS) was carried out with a Model VersaSTAT 3 electrochemical system (Princeton Applied Research, USA), and it was recorded with a frequency range from 10$^4$ to 0.1 Hz at a potential of 0 V. The characterize of CCNTs/GCE

**Preparation of CCNTs/GCE**

Prior to use, the GCE was polished successively on chamois leather with 0.3 and 0.05 μm Al$_2$O$_3$ slurry, followed by washing with HNO$_3$ (1:1, v/v), ethanol, and doubly distilled water in an ultrasonic bath. For the preparation of CCNTs modified GCE, 4 μL of 1.0 mg/mL as-prepared CCNT was droped onto the GCE surface and dried in the air.

**Analytical procedure**

ECL measurements were carried out at room temperature in 0.1 mol/L PBS containing 0.05 mol/L K$_2$S$_2$O$_8$. A cyclic voltammetry was scanned in the range of −1.6 - 0 V at a scan rate of 100 mV s$^{-1}$, and the ECL signal was then recorded. The determination was based on the difference in the ECL intensities, $\Delta$I$_{\text{ECL}} = I_{\text{ECL,0}} - I_{\text{ECL}}$, where $I_{\text{ECL,0}}$ is the ECL intensity of CCNTs/GCE at −1.6 V in the absence of CV, while $I_{\text{ECL}}$ represents the ECL intensity of CCNTs/GCE at −1.6 V in the presence of various concentration of CV.

The water samples were obtained from a local fish farm, and were filtered by using a 0.22-μm membrane. Then, the water samples were used to make up a 0.1 mol/L PBS (pH 7.0) solution containing 0.05 mol/L K$_2$S$_2$O$_8$, 10 mg/mL N-GQDs and a certain concentration of CV. Finally, the obtained solution was analyzed as described above.

**Results and Discussion**

The characteristic of CCNTs/GCE

CNTs offering unique properties, such as good mechanical strength, large surface area, good conductivity, and chemical stability, which was widely applied in electrochemical sensing. After dealing with strong acid, the CNTs were broken and separated from each other. Meanwhile, the C-atom was oxidized to the carboxyl group. Functionalized with carboxylic group can change the hydrophobic nature of CNTs, and the obtained CCNTs showed good dispersion ability and binding activity. Meanwhile, the COOH groups on the CNT surface play an important role in the electron transfer. From the SEM morphology (Fig. 1), it can be seen that the CCNTs have a large net-like and tube-like interlaced structure which suffers large surface area.

Modifying with CCNTs obviously promoted the electrochemical properties of GCE. Figure 2A exhibits the cyclic voltammogram curves of bare GCE and CCNTs/GCE, the current intensities of the redox peak of CCNTs/GCE were larger than that of GCE, and meanwhile the potential difference decreased. The phenomenon was caused by the acceleration role of CCNTs for electron transfer. The EIS results further convinced the CCNTs activities, as shown in Fig. 2B. The transfer resistance ($R_t$) of the electrodes can be obtained from the semicircular diameter which responds to the changes of the electrode-solution interface. As shown in Fig. 2B, the Nyquist diagram of CCNTs/GCE ($R_t = 45.0$ Ω) significantly decreased compared to that of bare GCE ($R_t = 94.6$ Ω), indicating that the introduction of CCNTs remarkably improves the electron transfer between the modified electrode and the electrolyte.

The ECL behaviors of N-GQDs@S$_2$O$_8^-$ system

The ECL behaviors of GCE and CCNTs/GCE in different systems were observed in 0.1 mol/L PBS (pH 7) under the
potential range of $-1.6 - 0$ V. It can be seen in Fig. 3, a weak ECL peak occurred at GCE in presence of N-GQDs (curve a), indicating that the ECL activities N-GQDs is very low. The additional K$_2$S$_2$O$_8$ resulted in an obvious enhancement of the ECL intensity at GCE (curve b). As the negative potential was applied, N-GQD and S$_2$O$_8^{2-}$ formed the reduced species of N-GQD*– (Eq. (1)) and oxidized species of SO$_4^{2-}$ (Eq. (2)), respectively. Then, the interaction between N-GQD* – and SO$_4^{2-}$ caused the formation of the radical N-GQD* (Eq. (3)), which was successively decay back to N-GQDs and generate ECL emission (Eq. (4)).

$$\text{N-GQDs} + e^- \rightarrow \text{N-GQD}^*,$$ (1)

$$\text{S}_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{*},$$ (2)

$$\text{N-GQD}^* + \text{SO}_4^{2-} \rightarrow \text{N-GQD}^* + \text{SO}_4^{2-},$$ (3)

$$\text{N-GQD}^* \rightarrow \text{N-GQDs} + h\nu.$$ (4)

The ECL signal of N-GQDs@S$_2$O$_8^{2-}$ was significantly amplified at CCNTs/GCE (curve c); the intensity was about 21-fold larger than that at bare GCE. The modified CCNTs provided enormous specific surface area for the ECL reactions and resulted in a significant promotion of electron transfer for ECL process. With the addition of 5.0 μmol/L CV, the ECL signal from N-GQDs* was remarkably decreased (cf. Fig. 3, curve d). The quenching phenomenon was probably due to the consumption of the radical N-GQDs* by electron transfer from the radical N-GQDs* to CV. Figure 4 represents the quenching mechanism of CV on the ECL signal of CCNTs/GCE and N-GQDs@S$_2$O$_8^{2-}$ system.

### Study of experimental conditions

The effects of experimental parameters including modified CCNTs amount, solution pH, and scan rate, on the ECL intensity have been investigated in order to maximize the detection sensitivity. With increasing amount of CCNTs (Fig. 5A), the ΔECL firstly increased and reached its maximum when CCNTs amount reached 4 μL, and then suddenly decreased at 5 μL CCNTs. CCNTs offered a large surface area for the ECL reaction and apparently accelerated the electron transfer. However, the increase thickness of modified CCNTs film would cause an increase in the internal resistance of CCNT, which hinder the electron transfer between the CCNTs surface and GCE, and thereby resulted in the decrease of the ECL intensity. Therefore, 4 μL CCNT amount was chose to modify the GCE.

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**Fig. 2** (A) Cyclic voltammogram curves of GCE and CCNTs/GCE in 0.1 mol/L NaCl containing 5 mmol/L K$_3$[Fe(CN)$_6$]//K$_4$[Fe(CN)$_6$]. (B) Nyquist plots of the EIS for bare GCE and CCNTs/GCE in 0.1 mol/L NaCl solution containing 5 mmol/L K$_3$[Fe(CN)$_6$]//K$_4$[Fe(CN)$_6$] with a frequency range from 10$^5$ to 0.1 Hz at a potential of 0 V.

**Fig. 3** ECL-potential curves of bare GCE and CCNTs/GCE in 0.1 mol/L PBS (pH 7.0) containing different ECL system; a, GCE + N-GQDs; b, GCE + N-GQDs@S$_2$O$_8^{2-}$; c, CCNTs/GCE + N-GQDs@S$_2$O$_8^{2-}$; d, CCNTs/GCE + N-GQDs@S$_2$O$_8^{2-}$ + CV. The concentration of K$_2$S$_2$O$_8$, N-GQDs, and CV concentrations were 0.05 mol/L, 10 mg/mL, and 5.0 μmol/L, respectively. Scan rate: 100 mV/s.

**Fig. 4** Quenching mechanism of CV on the ECL signal of the CCNTs/GCE and N-GQDs@S$_2$O$_8^{2-}$ system.
The effect of the solution pH on $\Delta I_{ECL}$ was studied in the pH range of 5 – 9 (Fig. 5B). It could be observed that the $\Delta I_{ECL}$ intensity achieved the maximum value at pH 7. In the acidic condition, $S_2O_8^{2-}$ is apt to reduce to the intermediate species of $SO_4^{*}$ in higher pH. However, the decrease of ECL intensity at alkaline solution was caused by the reduction of the oxidant $S_2O_8^{*}$ via the scavenging effect of OH$^–$. Thus, the solution pH was adjusted to 7.0 for the determination.

The formation rate of N-GQDs* and the ECL intensity were affected by the scan rate as well. Figure 5C showed the changes in $\Delta I_{ECL}$ with increasing of scan rate. At first, the $\Delta I_{ECL}$ firstly increased from 25 – 100 mV/s due to the formation rate of N-GQDs* increased accordingly. At a high scan rate, the consumption of coreactant on the electrode interface is much faster than the diffusion of the coreactant from the bulk solution to the electrode surface, causing a low transient concentration of $S_2O_8^{2-}$ near to the electrode surface, accompanied by a decrease in the ECL intensity at 125 mV/s. Hence, the scan rate was set as 100 mV/s.

**Linear range and detection limit**

The sensor of CCNTs/GCE associating with the N-GQDs@$S_2O_8^{2-}$ ECL system were employed to determine the CV under the optimal conditions. With increasing concentration of CV, the ECL signals were gradually declined (Fig. 6A), and the quenched ECL intensity ($\Delta I_{ECL}$) was found to be linear with the logarithm of CV concentration from 0.05 to 50 μmol/L ($\Delta I_{ECL} = 3646.4 \lg C + 6149.83$), with a correlation coefficient of $r = 0.9905$. The limit of detection (LOD) was evaluated as 45 nmol/L ($S/N = 3$). As shown in Table 1, the proposed ECL method displayed a satisfactory detection limit compared to the most commonly used methods.

**Interference and reproducibility**

The interferences that commonly coexist in the fishpond water including sodium salts, ammonium salts, and sugars were also detected by the proposed system in order to investigate the selectivity of the sensor. The results showed that no interference took place in the presence of the following substances: 200-fold concentration of fructose, 500-fold NaCl, NH₄Cl, and Na₂SO₄.
based on CCNTs/GCE associating with the N-GQDs@S2O82– (pH 7) containing 10 mg/mL N-GQDs and 0.05 mol/L K2S2O8. The ECL system was constructed for the determination of CV. The results exhibited a great potential application for real sample analysis.

| Sample 1 | Added/μmol L–1 | Detected/μmol L–1 | Average/μmol L–1 | Recovery, % | RSD, % |
|----------|----------------|-------------------|------------------|-------------|--------|
| 0.075    | 0.073          | 0.072             | 0.077            | 98.67       | 3.58   |
|          | 1.00           | 1.12              | 1.12             | 112.00      | 4.93   |
|          | 5.00           | 5.09              | 5.03             | 100.60      | 1.45   |

The fishpond samples obtained from the local fish farm were used to assess the practical application of the proposed method. Recovery testing was carried out to demonstrate the validity of the ECL system. As shown in Table 2, the obtained recoveries of three samples were 98.67, 112.00, and 100.60%. The average relative standard deviation (RSD) of the three samples was less than 5%, indicating that the proposed ECL method has good accuracy and might be able to be applied in the analysis of real samples.

### Sample analysis

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### Conclusion

In the present work, a simple and valid ECL method which based on CCNTs/GCE associating with the N-GQDs@S2O82– system was constructed for the determination of CV. The ECL intensities were significantly amplified by CCNTs, causing the increase of analytical sensitivity. With the presence of low concentration of CV, a high quenching effect on the ECL signal appeared and the quenched ECL intensity exhibited good linearity in the range from 0.05 to 50 μmol/L CV. The results represent a wide detection range, low detection limit, and good responsibility and selectivity. Meanwhile, the proposed method exhibited a great potential application for real sample analysis.

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