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# Electrochemical detection of heavy metals and chloramphenicol using a nafion/graphene quantum dot modified electrode

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**Abstract:** Graphene quantum dots (GQDs) with a uniform particle size were successfully synthesized using a simple in-situ electrolytic graphite rod method at a specific current density. Nafion/GQD-modified glassy carbon electrodes (nafion/GQDS/GCE) were then fabricated. Anodic stripping voltammetry and differential pulse voltammetry were utilized for the detection of heavy metals, specifically Pb(II) and Cd(II), as well as chloramphenicol. The results indicated that the dissolution currents for Pb(II) and Cd(II) increased with their concentrations, showing a strong linear relationship. The linear range for Pb(II) was  $4.82 \times 10^{-8}$  to  $9.65 \times 10^{-7}$  mol/L ( $R^2 = 0.9923$ ), and for Cd(II), it was  $1.07 \times 10^{-7}$  to  $1.96 \times 10^{-6}$  mol/L ( $R^2 = 0.9912$ ), with detection limits of  $1.61 \times 10^{-8}$  mol/L for Pb(II) and  $3.57 \times 10^{-8}$  mol/L for Cd(II). The nafion/GQDS/GCE exhibited significant electrocatalytic activity towards chloramphenicol, with an irreversible reaction involving 6 electrons and an electron transfer rate constant (KS) of  $105.4 \text{ s}^{-1}$ . The catalytic reduction current for chloramphenicol at the modified electrode ranged from  $5.00 \times 10^{-7}$  to  $2.50 \times 10^{-3}$  mol/L, showing a good linear relationship, and the detection limit (S/N = 3) was  $1.67 \times 10^{-7}$  mol/L. The nafion/GQDS/GCE also demonstrated excellent anti-interference, stability, and reproducibility, yielding satisfactory results for the detection of actual samples.

**Keywords:** graphene quantum dots; chloramphenicol; modified electrode; heavy metals; differential pulse voltammetry

Heavy metals are common pollutants in drinking water, especially Pb(II) and Cd(II). Pb(II) and Cd(II) pollution have high stability. Non degradability. Accumulation and other characteristics. Exposure to a certain dose of Pb(II) and Cd(II) through drinking water can lead to a variety of negative health effects and serious harm to human health. In 2006, China promulgated and implemented the new hygienic standard for drinking water (GB5749-2006), which stipulates that the limit concentration of Pb(II) is 0.01 mg/L, and the limit concentration of Cd(II) is 0.005 mg/L [1]. Chloramphenicol (CAP) is a broad-spectrum antibiotic with strong bactericidal power, which is widely used in the treatment of various bacterial infectious diseases in animals, mainly tablets and capsules. Eye drops, ear drops, etc. Cap drug residues will affect the human hematopoietic system. The digestive system produces serious toxic reactions, and many countries have expressly prohibited the use of cap in foodborne animals. Therefore, in the field of food and drugs, the quantitative analysis of cap has important practical significance for quality monitoring and ensuring the health of consumers.

At present, the main analytical methods for the determination of Pb(II) and Cd(II) are atomic spectrometry [2] and electrochemical analysis [3]. The main determination methods of cap are high performance liquid chromatography [4].

Raman spectroscopy [5]. Fluorescence spectroscopy [6] and electrochemical methods [7], etc. Electrochemical method is simple to operate. Fast and sensitive. Low cost. More and more attention has been paid to environmental friendliness and field analysis. However, the existing electrochemical detection methods of heavy metals and cap still have some shortcomings, such as poor detection sensitivity. Insufficient anti-interference. Lack of stability and other problems. Therefore, the development sensitivity is high. New electrochemical detection methods with good selectivity and convenient operation have important research significance.

Graphene quantum dots (GQDs) usually refer to zero dimensional carbon nanomaterials with particle size less than 10 nm. As a new carbon nano material, GQDs not only has the high conductivity of graphene. Large specific surface area, combined with the size effect of quantum dots. The advantages of confinement effect and edge effect make it widely used in biomedicine. Sensors. Optical and electrical devices have been widely studied [8]. But GQDs is applied to Pb(II). However, the sensitive detection of CD(II) and cap has not been reported.

In this paper, GQDs were prepared by simple in-situ electrolysis of graphite rods, and Nafion/GQDs modified glassy carbon electrodes (Nafion/GQDs/GCE) were constructed. Nafion/GQDs/GCE was applied to trace Pb(II) in water. Detection of CD(II) and cap in drugs, and study the electrochemical behavior and electrocatalysis mechanism of Nafion/GQDs/GCE. The results show that Nafion/GQDs/GCE is effective for Pb(II). The detection of CD(II) and cap has excellent electrochemical performance and high sensitivity. Good anti-interference performance. It has been applied to the detection of actual samples and achieved satisfactory results.

## 1. Experimental part

### 1.1. Instruments and reagents

Chi660d electrochemical analyzer (Shanghai Chenhua Instrument Co., Ltd.). Three electrode system: working electrode (GCE AS substrate), reference electrode Ag/AgCl (saturated nacl) and auxiliary electrode platinum wire. Jem-2100 transmission electron microscope (TEM) (JEOL company, Japan). QM/TM fluorescence spectrometer (proteintechnologies, USA).

1000 mg/LPb(II) and CD(II) standard solutions (China National Institute of certified reference materials); 5% Nafion (sigma ADL rich); EDTA,  $K_3[Fe(CN)_6]$ ,  $K_4[Fe(CN)_6]$ ,  $Na_2HPO_4$ ,  $KH_2PO_4$ ,  $NaHCO_3$ , KCl, NaOH,  $HNO_3$ , HAc, NaAc. 85% hydrazine hydrate and chloramphenicol (Sinopharm Chemical Reagent Co., Ltd.); tetracycline hydrochloride. Tetracycline chloride. Kanamycin. Ibuprofen. Terramycin (Beijing bailingwei Technology Co., Ltd.); TE buffer solution (pH = 7.0, biotechnology (Shanghai) Co., Ltd.); graphite rod (Shanghai SANSU Industrial Co., Ltd.); dialysis bag (3500Da, EXP2019/06, USA). All chemicals are premium grade. The experimental water is deionized water.

## 1.2. GQDs preparation

GQDs were prepared by anodic electrolysis of graphite rods [9] and improved. The graphite rod is used as the working electrode (anode), and the platinum sheet is used as the auxiliary electrode, which is placed in 7 mL 0.1 mol/L NaOH solution. Chronoamperometry is adopted, and the initial potential is  $-5$  v. High potential  $+5$  v. The low potential is  $-5$  v, and the current density of the control electrode is  $30\sim 50$  ma/cm<sup>2</sup>. After power on, a large number of bubbles were immediately generated on the surface of the graphite rod electrode. Soon, it was seen that there were very fine black substances falling near the graphite rod electrode. The electrolytic solution changed from colorless to light brown in about 15 min, and gradually changed from brown to black in about 30 min. With the increase of electrolysis time, the color of the solution became darker and darker, and there were obvious black deposits at the bottom of the bottle. After continuous electrolysis for 6 h, transfer 1 mL of 85% hydrazine hydrate into the electrolytic solution system and stir for several hours. Transfer the stirred solution to the purified dialysis bag, seal both ends of the dialysis clip, put an appropriate amount of deionized water for dialysis for 24 h to obtain neutral GQDs aqueous solution, and dry at constant temperature at  $40$  °C to obtain solid GQDs.

## 1.3. Preparation of Nafion/GQDs/GCE

After grinding GCE on W<sub>7</sub> metallographic sandpaper, use  $0.05$   $\mu$ L Al<sub>2</sub>O<sub>3</sub> suspension is polished on suede to form a mirror, and then on HNO<sub>3</sub> (1 + 1) in turn. Ultrasonic for 5 min in ethanol and water respectively, and air dry for use. Weigh 10 mg of GQDs, put it in 5 mL of 0.5% Nafion ethanol solution, and disperse it by ultrasound for more than 30 min to form a uniform black suspension. Add 10  $\mu$ L Nafion/GQDs/GCE was prepared by putting ethanol solution of 12mg/ml Nafion/GQDs on the surface of GCE. Nafion/GCE was prepared according to the above method, but GQDs was not added.

## 1.4. Pb(II) and Cd(II) anodic stripping voltammetry detection

Take 10 mL HAc-NaAc buffer solution (pH = 4.5), add an appropriate amount of Pb(II) and Cd(II) standard solution, place it in the electrolytic cell, and detect it by anodic stripping voltammetry. The deposition potential is  $-1.0$  V, and the deposition time is 240 s. At the end of enrichment, after 10 s of rest, scan from negative to positive at the potential of  $-1.0\sim 0$  V, and the metal ions dissolve. After each dissolution, set the potential  $e = +0.1$  V and clean the electrode surface for 30 s. In the process of deposition and cleaning, the solution is stirred, and the solution is not stirred in the dissolution process.

## 1.5. Electrochemical detection of cap

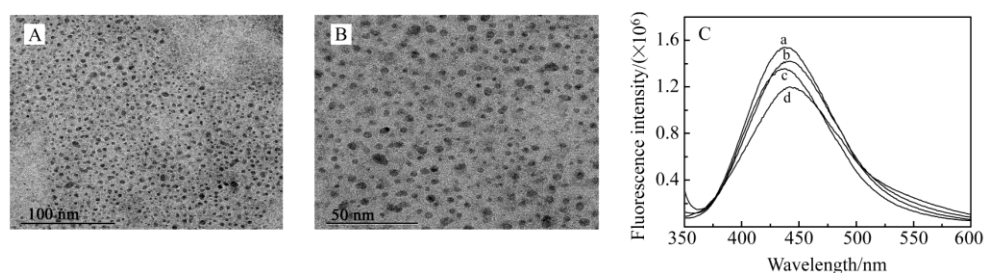
Using TE buffer solution (pH = 7.0) as electrolyte, the electrochemical performance and behavior of Nafion/GQDs/GCE for cap detection were characterized by cyclic voltammetry. The scanning potential range is  $-0.3\sim -1.2$  V, and the scanning speed is 50 mV/s. Differential pulse voltammetry was used for electrochemical detection of cap. Scanning potential is  $-0.3\sim -1.2$  V, pulse increment

is 0.004 V, pulse amplitude is 0.05 V, and pulse width is 0.2 S.

## 2. Results and discussion

### 2.1. Transmission electron microscope and fluorescence spectrum characterization of GQDs

**Figure 1** shows the transmission electron microscope (TEM) and fluorescence spectrum of GQDs. It can be seen from **Figure 1A,B** that GQDs prepared by electrolytic graphite rod have uniform particle size, good dispersion, no clustering and stacking, and the average diameter is less than 10 nm. **Figure 1C** shows the fluorescence spectra of GQDs in ethanol at different excitation wavelengths. It can be seen that the ethanol solutions of GQDs are at 310, 320, 330. Under the excitation of 340 nm wavelength, the measured fluorescence peak position is about 430 nm, that is, the peak intensity is not affected by the excitation wavelength, which proves that the particle size of GQDs is relatively uniform and well dispersed [10]. The luminescence intensity at different excitation wavelengths first increases and then decreases with the increase of wavelength. The fluorescence intensity of GQDs is the largest at 320 nm excitation wavelength. According to the literature report [10], the position where the maximum fluorescence intensity appears can be inferred that GQDs emit blue fluorescence and have the properties of carbon quantum dots.



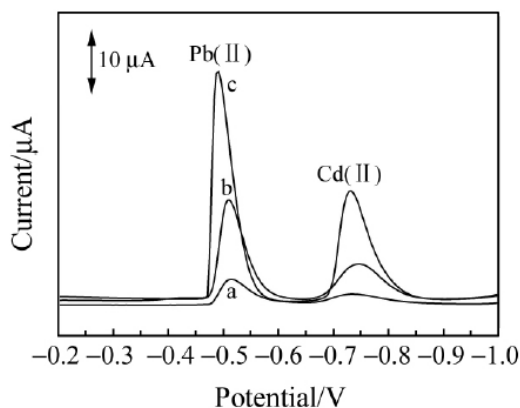
**Figure 1.** TEMI images of (A) low; and (B) high magnification of GQDs; (C) fluorescence spectra of GQDs (the excitation wavelength: a) 320 nm, b) 310 nm, c) 330 nm and (d) 340 nm).

### 2.2. Nafion/GQDs/GCE applied to electrochemical detection of Pb(II) and CD(II)

#### 2.2.1. Anodic stripping voltammetric detection of Pb(II) and CD(II) at different electrodes

**Figure 2** shows the anodic stripping voltammetry of Pb(II) and CD(II) detection at different electrodes. It can be seen from the figure that the dissolution peaks of Pb(II) and CD(II) on bare GCE are very small, especially insensitive to CD(II); Pb(II) and CD(II) have sensitive dissolution peaks on Nafion/GCE, and the dissolution potentials are  $-0.52$  v and  $-0.75$  v, respectively. It can be seen that Nafion is a cation exchanger, and  $-\text{SO}_3\text{H}$  on the surface of Nafion membrane is conducive to the metal ions in the test solution close to the electrode surface. Through ion exchange, the purpose of more effective enrichment of metal ions is achieved, thereby increasing the dissolution current [11]. However, when GQDs were introduced, Pb(II) and CD(II) were the most sensitive in Nafion/GQDs/GCE.

For the sharpest dissolution peak, the peak current increases greatly, and the peak potential shifts slightly, which are  $-0.50$  v and  $-0.73$  v respectively. It is proved that GQDs effectively increases the active area and electron transfer rate of the electrode, thereby significantly increasing the oxidation dissolution current. In conclusion, the ion exchange effect of Nafion membrane promotes the enrichment of metal ions, but the Nafion membrane is not conductive, and the strong conductivity of godds is conducive to the electron/ion transfer rate of Nafion/GQDs electrode, thereby promoting the enrichment efficiency; in addition, the Nafion film disperses GQDs well, which makes it evenly distributed on the electrode surface, avoids clustering and loss, and is conducive to improving the stability of the electrode. At the same time, GQDs increases the electroactive area and electrochemical performance of Nafion/GQDs electrode. The synergy of the two greatly improves the analytical sensitivity of the electrode.



**Figure 2.** Anode stripping voltammograms of  $2.40 \times 10^{-7}$  mol/L Pb(II) and  $9.80 \times 10^{-7}$  mol/L Cd(II) at a: the bare GCE; b: Nafion/GCE; and c: Nafion/GQDs/GCE.

### 2.2.2. Influence of enrichment potential and enrichment time

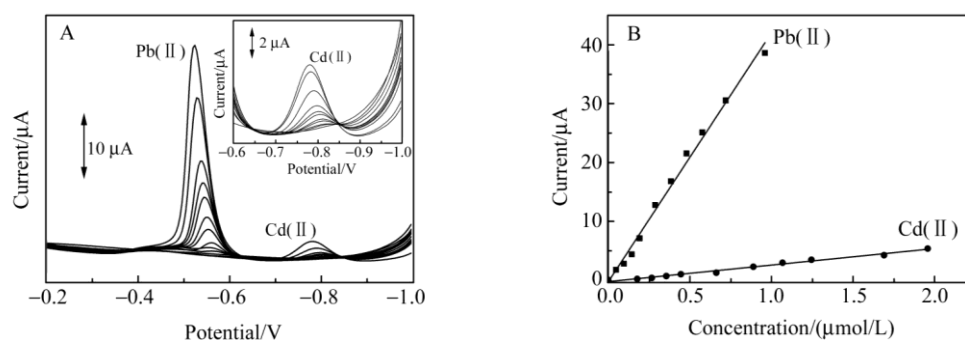
The effect of enrichment potential on the dissolution current of Pb(II) and CD(II) was investigated. With the increase of enrichment potential in the range of  $0.8 \sim -1.0$  v, the dissolution current of Pb(II) and CD(II) also increases, and  $-1.0$  v reaches the maximum. However, when the potential exceeds  $-1.0$  v, the enrichment current decreases. The possible reason is that the enrichment potential is too positive and the reduction of metal ions is not complete; if the potential is too negative, bubbles appear on the electrode surface, which is not conducive to the reduction reaction and affects the dissolution current. In this experiment, the optimized enrichment potential is  $-1.0$  v.

The effect of enrichment time on the dissolution current of Pb(II) and CD(II) was investigated. In the range of  $60 \sim 360$  s, the peak current of dissolution increased with the increase of enrichment time, and showed a good linear relationship. However, after more than 400 s, the peak current and enrichment time deviate from linearity, and the dissolution current increases slowly. The possible reason is that the enrichment time is too long and the electrode surface reaches saturation. Long time enrichment will lead to “passivation” on the surface of Nafion/GQDs/GCE and affect the sensitivity. However, the enrichment time is too short and the ions to be

measured in the solution system are not fully enriched, which affects the accuracy and reproducibility of the method. The optimized enrichment time in this experiment is 240 s.

### 2.2.3. Quantitative detection of Pb(II) and Cd(II) by Nafion/GQDs/GCE

**Figure 3** shows the differential pulse voltammetry of Nafion/GQDs/GCE for the continuous determination of Pb(II) and Cd(II) at different concentrations. According to the optimized experimental conditions, the dissolution current of Pb(II) and Cd(II) increased with the increase of Pb(II) and Cd(II) concentration. The peak current of Pb(II) has a good linear relationship with its concentration in the concentration range of  $4.82 \times 10^{-8} \sim 9.65 \times 10^{-7}$  mol/L. The linear equation is:  $y = 42.39x - 0.319$  ( $R^2 = 0.9923$ ), and the detection limit is  $1.61 \times 10^{-8}$  mol/L; The peak current of Cd(II) has a good linear relationship with its concentration in the concentration range of  $1.07 \times 10^{-7} \sim 1.96 \times 10^{-6}$  mol/L. The linear equation is:  $y = 2.813x - 0.283$  ( $R^2 = 0.9912$ ), and the detection limit is  $3.57 \times 10^{-8}$  mol/L. The detection limit of this method is lower than the limit standard of Pb(II) (0.01 mg/L) and Cd(II) (0.005 mg/L) in the hygienic standard for drinking water. It is also better than graphene modified platinum electrode [12] and graphene oxide/polydimethylsiloxane [13]. Silver nanoparticles/reduced graphene oxide [14]. Electrochemical detection of Pb(II) and Cd(II) at graphene oxide/antimony film [15] and other modified electrodes.



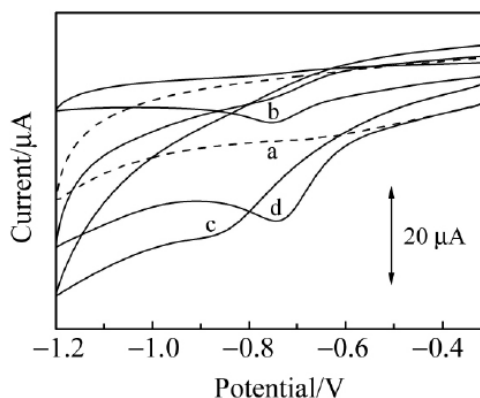
**Figure 3.** (A) different pulse voltammograms of Pb(I) and Cd(I) at the Nafion/GQDs/GCE; (B) linear plots of Pb(I) and Cd(I) stripping currents vs. concentrations.

## 2.3. Nafion/GQDs/GCE applied to electrochemical detection of cap

### 2.3.1. Electrochemical detection of cap with different electrodes

**Figure 4** shows different electrode pairs Cyclic voltammogram of  $1.0 \times 10^{-4}$  mol/L cap detection. It can be seen from the figure that Nafion/GQDs/GCE has no redox peak in the blank buffer solution. The bare GCE has a weak electrocatalytic reduction effect on the detection of  $1.0 \times 10^{-4}$  mol/L CAP in the process of scanning to the negative potential, and the peak potential is about  $-0.75$  V. No oxidation peak appeared in the positive potential scanning, indicating that the electrocatalysis of cap in bare GCE is an irreversible reaction. However, the electrocatalytic reduction signal of cap by Nafion/GCE was even worse, and the peak potential moved negatively to  $-0.88$  V. The reason is that Nafion film is not conductive, which hinders the electron transfer of cap on the surface of the electrode, resulting in

weaker electrocatalytic performance of the electrode. However, when GQDs was introduced into Nafion/GCE, the electrocatalytic performance of cap on the electrode was significantly improved, and the peak potential was moving to  $-0.72$  V, indicating that GQDs had a larger specific surface area and better electroactive sites, which promoted the catalytic reduction of cap on the surface of Nafion/GQDs/GCE, showing the strongest peak current.



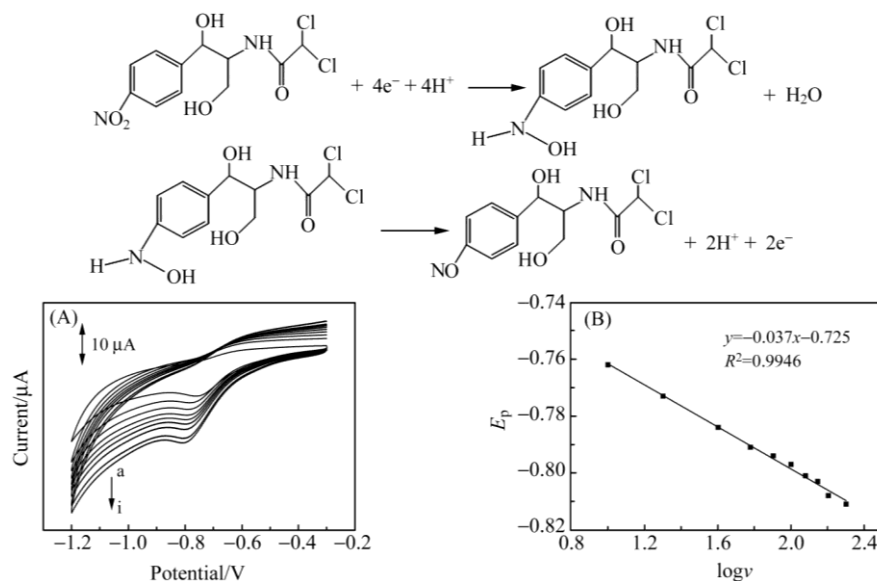
**Figure 4.** a: cyclic voltammograms of 0 mol/L and b:  $1.0 \times 10^{-4}$  mol/L CAP in TE buffer solution (pH = 7.0) at the bare GCE, c: Nafion/GCE; and (a, d): Nafion/GQDs/GCE.

### 2.3.2. Electrochemical behavior of Nafion/GQDs/GCE for cap detection

**Figure 5A** shows the cyclic voltammogram of Nafion/GQDs/GCE versus cap at different scanning speeds. With the increase of scanning rate, the catalytic current of cap on Nafion/GQDs/GCE gradually increases, and there is a good linear relationship between the reduction peak current and scanning rate in the range of 10~200 mv/s, which proves that the electrode reaction process is controlled by adsorption. With the increase of scanning rate, the peak potential gradually moves negatively, and the relationship between EP and  $\log v$  is:  $e_{pc} = -0.037 \log v^{-0.725}$  ( $r = 0.9946$ ). According to Laviron theory, when the system is an irreversible system, whose peak current is controlled by adsorption, the relationship between EPC and sweep velocity  $V$  is as follows:

$$E_{pc} = E_0 + \frac{RT}{\alpha nF} \ln \frac{RTk_s}{\alpha nF} - \frac{RT}{\alpha nF} \ln v \quad (1)$$

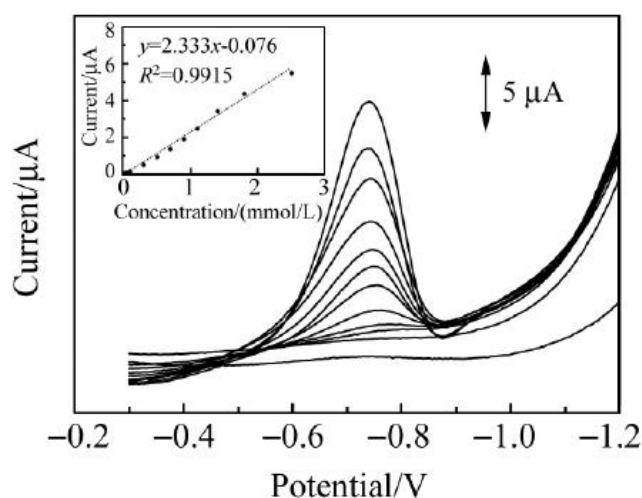
where  $R$  is the gas constant;  $F$  is Faraday constant;  $N$  is the number of electron transfers;  $T$  is the temperature, generally 298 K. Irreversible reaction,  $0 < \alpha < 1$ , so we get  $n = 6$ , that is, the electron transfer number is 6. From EPC-V curve and extrapolation method,  $e_0 = -0.766$  v can be obtained, and then the electron transfer rate constant  $k_s = 105.4 \text{ s}^{-1}$  of cap electrochemical reaction in surface adsorption state can be obtained. Based on the above discussion, the electro catalytic reduction mechanism of cap is speculated as follows [16,17]:



**Figure 5.** (A) cyclic voltammograms of  $1.0 \times 10^{-4}$  mol/L CAP at the Nafion/GQDs/GCE (scan rates (a→i): 10, 40, 60, 80, 100, 120, 140, 160, 200 mv/s); (B) linear plot of reduction potential vs.  $\log v$ .

### 2.3.3. Differential pulse voltammetric detection of cap by Nafion/GQDs/GCE

**Figure 6** shows the differential pulse voltammetry of Nafion/GQDs/GCE for continuous detection of cap. It can be seen from the figure that the reduction peak current of cap increases with the increase of its concentration, and there is a good linear relationship in the range of  $5.0 \times 10^{-7}$ ~ $2.5 \times 10^{-3}$  mol/L, and the detection limit is  $1.67 \times 10^{-7}$  mol/L. It is proved that the Nafion/GQDs/GCE modified electrode has a wide linear range and acceptable sensitivity for the detection of cap, which is better than graphene oxide/polyaniline [18]. Polydopamine peroxide [19]. Porous carbon/polydopamine [20]. The performance of nano cobalt [21] modified electrode for the detection of chloramphenicol is expected to be used for the quantitative detection of cap in actual samples.



**Figure 6.** Differential pulse voltammogram for the detection of CAP from  $5.0 \times 10^{-7}$  mol/L to  $2.5 \times 10^{-3}$  mol/L at the Nafion/GQDs/GCE.



#### 2.4. Anti interference performance of Nafion/GQDs/GCE

Different ions have different effects on the dissolution current of Pb(II) and Cd(II). It is found that the mass concentration is 100 times  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  anion has no effect on the electrochemical signals of Pb(II) and Cd(II). A variety of cations, such as Na(I), Ca(II), Mg(II), Al(III), K(I) does not interfere with the determination of Pb(II) and Cd(II) because it is chemically inert by voltammetry, Zn(II), Co(II), Ni(II). The redox voltage of Mn(II) is negative to that of Pb(II) and Cd(II) without interference [22]. The redox voltage of some cations is higher than that of Pb(II) and Cd(II), such as Cu(II), Ag(I), Fe(II), Fe(III), Mn(III), Bi(III) Hg(II), etc. If the ion has no chemical reaction with the target substances Pb(II) and Cd(II) in the process of electrodeposition, such as Ag(I), Fe(II), Fe(III), Mn(III) and others will dissolve out at their respective oxidation potentials and will not interfere with the accurate determination of Pb(II) and Cd(II) [23]. Cu(II) with a concentration of more than 10 times will reduce the dissolution signals of Pb(II) and Cd(II), mainly due to the formation of Cu Pb and Cu Cd intermediates during deposition, which is consistent with the results in the literature [24]. High concentrations of Hg(II) and Bi(III) (>500  $\mu\text{g/L}$ ) will improve the electrochemical detection signals of Pb(II) and Cd(II). Because at the deposition potential of  $-1.0$  v, Bi(III) and Hg(II) can also be reduced, and Hg(II) and Pb(II) and Cd(II) form amalgam on the surface of Nafion/GQDs, Hg (Pb) and Hg (Cd), Bi(III) and Pb(II) and Cd(II) form "alloy" [25], making Pb(II) and Cd(II) more easily enriched. Therefore, in the presence of high concentrations of Hg(II) and Bi(III) ions, the dissolution peak currents of both increase correspondingly.

In order to investigate the selectivity of Nafion/GQDs/GCE for CAP detection, different interfering compounds such as tetracycline hydrochloride, chlorotetracycline, kanamycin, ibuprofen and oxytetracycline were studied at  $5.0 \times 10^{-4}$  mol/L chlorine Current response to tetracycline. Research shows that tetracycline hydrochloride with 20 times the concentration. Tetracycline chloride. Kanamycin and ibuprofen have very weak reduction peak current in the range of  $-0.7 \sim -0.8$  V. Compared with the peak current of cap, the peak current of interferents is very small, and the current change is within 5%. 20 times the concentration of oxytetracycline showed obvious reduction peak current at 0.58 V, and there was no reduction peak in the range of  $-0.7 \sim -0.8$  V. This experimental condition did not interfere with the detection of cap, indicating that the Nafion/GQDs modified electrode has good anti-interference and selectivity.

#### 2.5. Repeatability and reproducibility of Nafion/GQDs/GCE

The relative standard deviations of the peak currents of Pb(II) and Cd(II) were measured 15 times consecutively in the same Nafion/GQDs/GCE in  $5.0 \times 10^{-7}$  mol/L Pb(II) and Cd(II) solutions (RSD) were 2.32% and 3.84%, respectively. The reproducibility between different electrodes was also investigated, and 10 different Nafion/GQDs/GCE were applied in  $5.0 \times 10^{-7}$  mol/L Pb(II) and Cd(II) solutions for detection. The RSDs of Pb(II) and Cd(II) current values are 3.53% and 4.87%.

The same Nafion/GQDs/GCE was continuously measured 15 times in  $5.0 \times 10^{-4}$  mol/L CAP solution, and the RSD of the reduction peak current was 4.30%.

After each CAP measurement of the electrode, the amperometric method (i-t) is used, a voltage of about  $-0.75$  V is applied, and the electrode is cleaned for a few seconds under stirring until the surface of the electrode reacts completely, so as to deal with the CAP adsorbed on the modified electrode. Electrode regeneration. 10 different Nafion/GQDs/GCE were applied in  $5.0 \times 10^{-4}$  mol/L CAP solution for detection, and the RSD of peak current obtained was 4.96%, which proved that the Nafion/GQDs/GCE had good reproducibility and good reproducibility. The stability is expected to be applied to the detection and analysis of actual samples.

## 2.6. Detection of actual samples

Take drinking water samples from a community in Songjiang District, Shanghai, and use filter membrane (diameter  $0.45 \mu\text{m}$ ) After filtration, take 3 mL and put it into the electrochemical detection cell, dilute it to 10 mL with 0.1 mol/L HAC NaAc buffer, adjust the pH to 4.5, and conduct quantitative analysis with standard addition method. The spiked concentration Pb(II) is 0.06, 0.12. Zero point one eight  $\mu\text{mol/L}$ ; the spiked concentration of CD(II) is 0.10, 0.15. Zero point two zero  $\mu\text{mol/L}$ . The recovery rate of Pb(II) is 97.3%–108.5%, and that of CD(II) is 95.2%–110.8%. The method has good accuracy.

Take 2 mL cap eye drops, add 8 mlte buffer solution, adjust the pH value to 7.0, and then add cap standard solutions of different concentrations, with the concentration of 0.1 respectively, 0.2, 0.3, 0.45 m mol/L. After calculation, the cap content before dilution is about 0.75 mol/L ( $n = 3$ , about 2.42 mg/mL), which is very close to the cap content of 2.5 mg/mL on the instruction manual of chloramphenicol eye drops. The spiked recovery of the sample is 92.8%–109.5%, indicating that the modified electrode can be used to detect the content of cap in actual samples.

## 3. Conclusion

In this paper, GQDs with good performance were prepared by in-situ electrolytic graphite rod method, and a Nafion/GQDs/GCE detection method for Pb(II) was developed. A new method of CD(II) and cap. The results show that Nafion/GQDs/GCE has excellent electrochemical properties for Pb(II). The electrochemical detection of CD(II) and cap has good results, showing a wide linear range. High sensitivity. The advantages of good anti-interference performance are Pb(II) in actual samples. The rapid detection of CD(II) and chloramphenicol provides a new method reference.

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**Conflict of interest:** The authors declare no conflict of interest.

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