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Simultaneous Determination of Three Nitroaniline Isomers by β-cyclodextrins (β-CDs) and Graphene Quantum Dots (GQDs) Composite Modified Glassy Carbon Electrodes

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Nitroaniline isomers as toxic and environmental pollutant, their detection and recognition is an important task. A novel electrochemical sensor based on β-cyclodextrins (β-CDs) and graphene quantum dots (GQDs) composite modified glassy carbon electrodes (β-CDs-GQDs/GCE) has been fabricated for detection and discrimination of three nitroaniline isomers simultaneously. The β-CDs-GQDs/GCE electrode were characterized by different electrochemical techniques. The three isomers exhibited obvious peak current and potential differences on the modified electrode by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Because of the selective formation of H-bonds between β-CDs-GQDs composites and three nitroaniline isomers, the electrochemical recognitions were achieved. Especially, this recognition method relies on not only the peak currents but also the different oxidation potentials. Furthermore, the satisfactory results were obtained for the three noxious nitroaniline isomers simultaneous detection in two pesticides practical samples, when this electrode was applied. The investigates results show that β-CDs and GQDs are suitable material for isomers sensor. Moreover, its applicability in environmental contaminants promises its great potential utility in the near future.

Keywords: Nitroaniline isomers, β-CDs-GQDs/GCE, Electrochemical recognition, Environmental Contaminants.

1. INTRODUCTION

With the growth of population and the acceleration of industrialization, the environmental contamination caused by organic pollutants has become a prominent problem in the world. As nitro-substituted derivatives of aromatic amines, nitroaniline isomers including 2-nitroaniline (2-NA), 3-nitroaniline (3-NA) and 4-nitroaniline (4-NA) are environmental contaminants related to anthropogenic activities, such as all kinds of dye, pesticides and herbicides [1,2]. Nitroaniline isomers have been listed in priority pollutants in many countries, account for their highly toxic nature and their suspected carcinogenic properties. Nitroaniline isomers are directly released to the environment as industrial wastes or indirectly released to the environment as degradation products of herbicides and pesticides [3,4]. After entering into the environment, these compounds can experience complex environmental transformations at trace level, which may cause potential harm to the environment. Moreover, nitro-substituted aromatic compounds have strong electron-absorbing groups and have poor biodegradability in the environment. In view of the potential hazards of these compounds to the environment, it is necessary to develop a simple, fast and sensitive method for analysis and to identify and quantify these nitroaniline isomers in environmental samples. Efficient recognition of isomers by convenient techniques and simple materials is of great interest in analytical science, pharmaceutics, and biochemistry [5,6]. A variety of analytical methods for the determination of the three NA isomers include solid-phase extraction (SPE) [7], high-performance liquid chromatography (HPLC) [8], and capillary electrophoresis (CE) [9] et al. Among many isomer recognition technologies, the electrochemical approach has drawn enormous attention because of the fact that it overcomes the shortcomings such as the time-consuming and high cost associated with conventional chromatography [10,11]. For a large variety of isomers analytes, it is suitable for detection and identification of electroactive isomers by the electrochemical method. In recent years, various nano-recognition materials have been designed for isomers recognition, it is a significant task for developing widely used and effective identification materials. Chen et al. proposed β-cyclodextrin /silver nanoparticle composite modified ITO electrode and investigated the nitroaromatic compounds in aqueous solution by square wave voltammetry [12]. At the same concentration, various isomers of nitroaromatic compounds show characteristic reduction peaks, which make them easily distinguished from each other. The selectivity was determined by the strength of the host-guest interaction between β-CD and the respective isomers. Moreover, the proposed sensor was also used successfully for determination of nitroaromatic compounds in natural water samples. Lin et al. constructed the electro-polymerization of 7-[(2,4-dihydroxy-5-carboxybenzene)azo]-8-hydroxyquinoline-5-sulfonic acid (DHCBAQS) at a graphene-nafion modified glassy carbon electrode (GCE) [13]. The novel poly-DHCBAQS/graphene-nafion/GCE was successfully applied for the analysis of the noxious nitroaniline isomers in water and sewage samples. However, many current methods only were used for detection of a signal isomer, few reports about simultaneous determination. Therefore, more new functionalized materials with strong recognition ability to nitroaniline isomers are needed.

Graphene quantum dots (GODs) is a new kind of carbon-based material, which are graphene sheets film with the size less than 100nm. Due to quantum confinement and edge effect, GODs show various attractive advantages [14-18]. However, due to the lack of selectivity, few studies have used graphene as an electrode. β-cyclodextrins (β-CDs) are a class of cyclic oligosaccharides featuring a hydrophobic inner cavity and a hydrophilic exterior [19,20]. Because of the special molecular structure, β-CDs could form an inclusion complex with various guest molecules and have been proved to be suitable for stereoselective discriminations [21,22]. Therefore, if the two kinds of materials could be composited, the isomer compounds will realize detection and recognition.

In paper, the β-CDs-GQDs were modified on glass carbon electrode by electrodeposition to explore the potential of an electrochemical sensor for the simultaneous detection of nitroaniline isomers. When the β-CDs-GQDs/GCE was explored for the detection of nitroaniline isomers, the electrochemical behaviors of nitroaniline isomers on the modified electrode have been studied by differential pulse voltammetry (DPV) or cyclic voltammetry (CV), the results demonstrate that the provided modified electrode has higher sensitive, better selective and faster speed for simultaneous recognition and determination of nitroaniline isomers. Furthermore, the satisfied experiments results were also obtained in practical samples.

2. MATERIALS AND METHODS

2.1. Materials and apparatus

All the chemicals were of analytical reagent grade and all solution were prepared using deionized (DI) water. Nitroaniline isomers were purchased from Macklin. β-CD was bought from j&k Chemical. Pure graphite powder was obtained from Sinopharm Group Shanghai Chemical Reagent Co., Ltd. $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and KCl were acquired from Sinoreagent.

Fourier transform infrared (FT-IR) spectra of the samples in the fange of 550 and 4000 cm were recorded in IFS120HR (Bruker, German). The morphologies of samples were investigated by transmission electron microscopy (TEM) on a TECNAI G2 TF20 (FEI, USA). Electrochemical measurements were carried out at room temperature (25 °C) on a CHI-660 electrochemical workstation in a conventional three-electrode system with a glassy-carbon electrode (GCE) or a modified GCE as the working electrode, platinum wire as the auxiliary electrode, and an Ag/AgCl electrode (SCE) as the reference electrode. The sensor was characterized by CV, EIS and DPV.

2.2. Fabrication of GQDs and β-CD-GQDs

GQDs were prepared from natural graphite by acid treatment and chemicalexfoliation. Some changes have been made according to the methods previously reported [23]. 1.0 g of graphite powder was added to a mixture of concentrated sulfuric acid (80 mL) and 65% nitric acid (20 mL). The solution was refluxed at 140℃ for 30 hours, then cooled at room temperature and diluted with deionized water (700 mL). The pH was adjusted to 7 by using 1 M NaOH solution. The final product solution was further desalted with a macroporous resin. The mixture was concentrated to 400 ml and then poured into a macroporous resin column by deionized water immersion. The resin was immersed in the mixed solution for 8 hours, and washed with deionized water until the SO_4^{2-} was not detected by $BaCl_2$ in the eluent. Thereafter, the eluent was collected and dried to obtain pure GQDs.

0.01 g GQDs was mixed with 0.10 g β-CDs, and 5 mL of deionized water was added to completely dissolve. The dispersion was β-CDs-GQDs composite solution.

2.3. Preparation of β-CDs-GQDs/GCE

Before modifying the electrode, GCE were polished with 1.0 and 0.05 mm Al_2O_3, respectively and washed with DI water. Next, GCE was immersed and ultrasounded in water and methanol for 5 minutes to remove residual alumina particles. After the electrode is dried at room temperature, the β-CDs-GQDs modified electrode was prepared by electrodeposition. The electrodeposition process is as follows: The electrode was immersed in GQDs:β-CDs (1:10) composites solution, and then scanned at a rate of 0.1 V s^{-1} in the potential range of -1.0~2.0 V for 20 cycles to obtain a β-CDs-GQDs/GCE. The preparation of β-CDs-GQDs/GCE with other mass rates obtained as same as above.

2.4. Electrochemical measurements of the modified electrodes

Electrochemical characterization of the bare GCE, GQDs/GCE and β-CDs-GQDs/GCE were performed by CV and EIS, and all the electrochemical experiments were perform with three electrode systems, where the working electrode was the bare and modified GCE, the counter electrode was platinum wire electrode, and the reference electrode was Ag/AgCl electrode. CV measurements were made in 5 mM $[Fe(CN)_6]^{4-/3-}$ with 0.1 M KCl at a scan rate of 0.1 mV s^{-1} in the range of -0.2-0.6 V. The EIS test of different surface modifications of GCE electrodes were carried out on in a 5.0 mM $[Fe(CN)_6]^{4-/3-}$ solution containing 0.1 M KCl at a frequency of 106 to 10^{-2} hz and a potential of 220 mv at ambient temperature.

The solution containing appropriate amounts of 2-NA, 3-NA and 4-NA, together with 0.10 M HCl solution with 0.10 M KCl, were transferred to the electrochemical cell. CV measurements were carried out by using the three electrodes. The CVs in the potential range of +2.0 V and -1.0 V were recorded at a scan rate of 0.1 V s^{-1}. All experiments were performed at room temperature.

2.5. Real samples analysis

For real samples analysis, the content of nitroaniline isomers in the two pesticide samples was determined on β-CDs-GQDs/GCE. Firstly, the samples were dissolved in 200 mL distilled water, stirred for 5 min and then the solution was filtered through a funnel to remove the filler and other loading agents and collected in a volumetric flask. The pesticide samples were collected and diluted to 5 mL, and a solution was formed with 0.1 ml of HCl and 0.1 ml of KCl. The diluted samples were stored at -20 ℃ before measurement.

3. RESULTS AND DISCUSSION

3.1. The characterization of the β-CDs /GQDs hybrid

GQDs were prepared according to the previous work [24]. FT-IR image of GQDs shows that, GQDs have a large number of oxygens containing groups. The characteristic peaks at 3330, 1661 cm^{-1} were existed. The band around 1729 cm^{-1} corresponds to C=O stretching vibrations from carbonyl and carboxylic groups. The bands around 1450 cm^{-1} was is caused by C-OH stretching vibrations. The FT-

IR spectra provides the evidence that different types of oxygen functional groups are present on GQDs materials. The TEM image of GQDs presented similar results to the previous work. The results of FT-IR and TEM show that the GQDs were fabricated successfully.

3.2. Characteriztion of β-CD-GQDs hybrids modified electrode

We used cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) to characterize the preparation and eletrochemical behavior of β-CD-GQDs/GCE. Fig.1 A showed the cyclic voltammograms of the GCE recorded in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1M KCl between scan potential -0.20 and 0.60 V at scan rate of 100 $mV \cdot s^{-1}$. The quasi-reversible oxidation peak can be obtained at bare GCE with ΔE_p = 89 mV and ΔI_p=403 μA. After electrodeposition of GQDs onto the surface of GCE, ΔE_p increased significantly to 472 mV, while ΔIp also decreased significantly to 191 μA, which was most likely due to the repulsion between the oxygen-containing groups on GQDs and the anions of $[Fe(CN)6]^{3-/4-}$. Compared with GQDs/GCE, the ΔE_p at the β-CDs-CQDs/GCE became relatively small (342mV) and ΔI_p rose to 230 μA [25,26]. This indicated that GQDs were encapsulated by β-CDs, then oxygen-containing groups on GQDs were covered, thereby reducing the repulsion of the anions in $[Fe(CN)6]^{3-/4-}$. The Fig. 1B exhibits the results of EIS of the bare GCE, GQDs/GCE and β-CD-GQDs/GCE in presence of 5.0 mM $Fe(CN)_6^{3-/4-}$ / 0.1M KCl. It can be seen that bare GCE displayed a semicircle part at high frequency. R_{ct} was estimated to be 69 Ω. After being modified with GQDs, the semicircle diameter of EIS increased and R_{ct} increased to 824 Ω, indicating that GQDs was deposited on GCE surface. After β-CD-GQDs hybrids modification, R_{ct} deceased to 721 Ω, indicating GQDs and β-CD hybrids had much better electrons transfer properties than GQDs. The results of EIS agreed well with those of CVs.

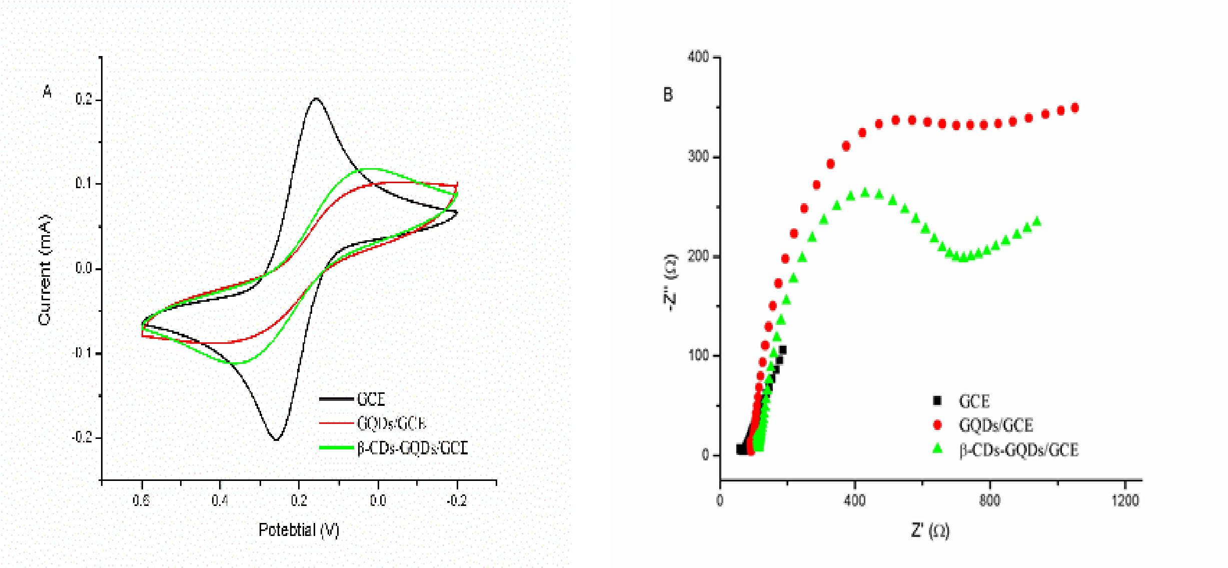

Figure 1. Cyclic voltammograms (A) and impedance plots (Nyquist plots) (B) obtained in 5 mM $[Fe(CN)_6^{3/4-}]$ for the bare GCE, GQDs/GCE, β-CDs-GQDs/GCE

3.3. Electrochmical behaviors of nitroanline isomers

The electrochemical behaviors of 2-NA, 3-NA and 4-NA on the β-CD-GQDs/GCE, GQDs/GCE and bare GCE were carefully investigated in 0.5 M phosphate buffer solution (pH 7.0). Fig. 2 shows the differential pulse voltammograms of 20 μg·mL^{-1} 2-NA, 3-NA and 4-NA at the different electrodes, respectively. At bare GCE, two of broad, unresolved oxidation peaks had been found at -0.112V and -0.472V, which suggested that the oxidation peaks of 2-NA, 3-NA and 4-NA could not be simultaneously detected at the bare GCE. While at the GQDs/GCE, three oxidation peaks (2-NA, 3-NA and 4-NA) with quite weak peak currents were presented at -0.064 V, -0.280 V and -0.396 V, respectively, which means that the oxidation peaks of those three nitroaniline isomers could be distinguished by a low electrochemical response. After modification by β-CD GQDS hybrids, the peak current of 2-Na, 3-Na and 4-Na further increased, and the oxidation peaks appeared at -0.064 V, -0.296 V and -0.450 V, respectively. Three well-defined oxidation peaks indicated that the simultaneous recognition of 2-NA, 3-NA and 4-NA could be achieved better.

The reason of the recognition may be due to the selective formation of H-bonds between β-CDs-GQDs composites and nitroaniline isomers. The recognition of nitroaniline isomers on bare GCE, GQDs/GCE and β-CDs-GQDs/GCE further validated this hypothesis because the recognition efficiency was significantly improved after the introduction of GQDs and β-CDs. The superior performance of β-CDs-GQDs/GCE can be attributed to the following reasons. Firstly, the three-dimensional structure of GQDs contained a large number of oxygen-containing groups, and the smaller size improved the electroactive region and facilitated the accumulation of the species.

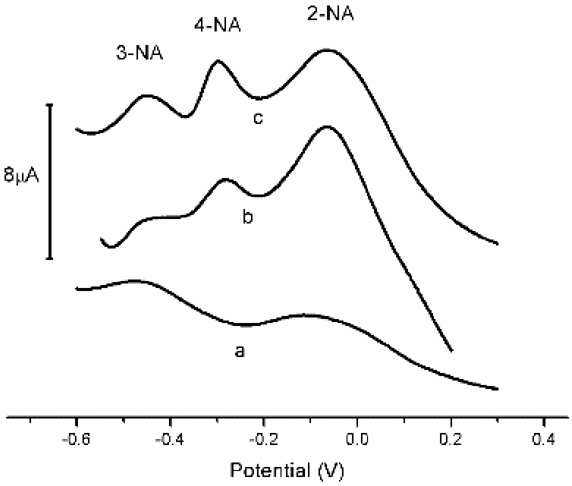

Figure 2. Differential Pulse voltammograms of the 20 μg·mL^{-1} 2-NA, 3-NA and 4-NA in PBS at different modified electrodes (0.1 M, pH 7.0): (a) bare GCE, (b) GQDs/GCE, (c) β-CDs-GQDs/GCE

Secondly, GQDs with large specific surface provided a large number of catalytic sites, which can form hydrogen bonds with three isomers. Thirdly, the large specific surface area of GQDs also provided a lot of catalytic sites to form hydrogen bonds with β-CDs, and a large numbers β-CDs attached to the surface of GQDs. Therefore, the host-guest recognition effect of β-CDs was brought into full play. To sum up, the synergistic effect of the above causes led to the separation and simultaneous determination of the three isomers.

3.4. Method verification

Further study on the quantitative measurements of nitroaniline isomers was performed by DPV. A series of known concentration of nitroaniline isomers were analyzed in PBS (0.1 M, pH 7.0) (Fig.3). Kept the two isomers in the concentration of 100 μg·mL^{-1} and the peak currents of the three compounds were directly proportional to analytical concentration of the other isomer in the range of 0.06~200 μg·mL^{-1}. Fig. 3 A displayed DPV responses of different concentration of 2-NA with a constant of 100 μg·mL-^{1} 3-NA and 4-NA. The results showed that the anodic peak current was linear to the concentration of 2-NA in the range of 0.06~200 μg·mL^{-1}. The regression equation was ip=1.853 + 0.319c (μg mL^{-1}, R^{2}=0.995) with a detection limit of 6.625 ×10^{-3} μg·mL^{-1} (S/N=3). Similarly, as observed in Fig. 3 B, keeping the concentration of 2-NA and 3-NA constant (100 μg mL^{-1}), the oxidation peak current increased linearly with increasing the concentration of 4-NA from 0.6 to 200 μg·mL^{-1}. A linear equation ip=0.273 + 0.035c (μg mL^{-1}, R^{2}=0.999) was obtained and the detection limit was 1.876 ×10^{-3} μg·mL^{-1} (S/N=3). 3-NA also got the regression equation was ip=0.433 + 0.015c (μg mL^{-1}, R^{2}=0.997) with a detection limit of 1.005 ×10^{-2} μg·mL^{-1} (S/N=3) (Fig. 3 C).

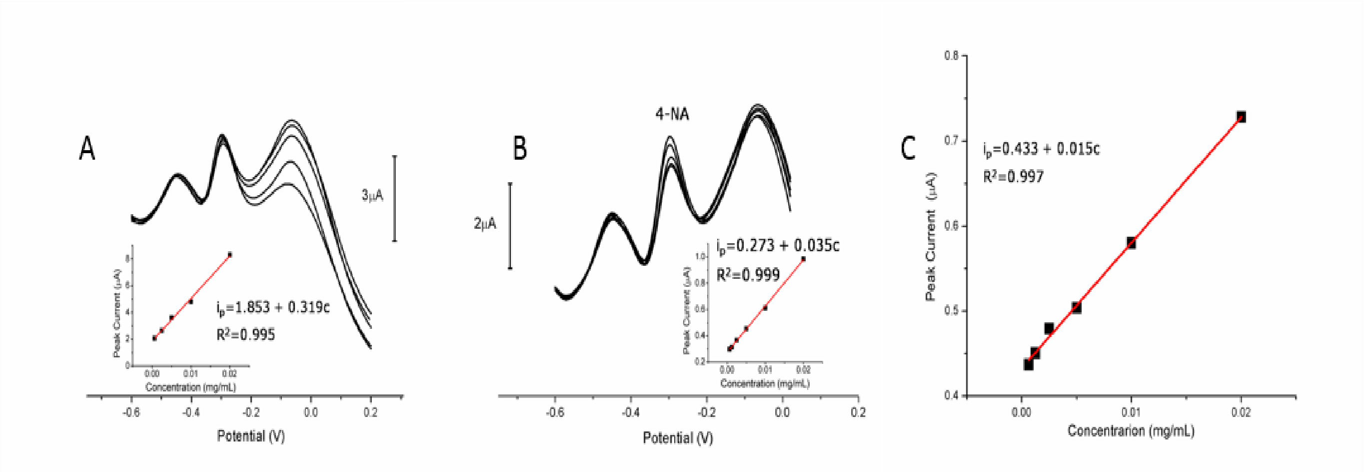

Figure 3. (A) DPV of β-CDs-GQDs/GCE in the presence of 100 μg·mL^{-1} 3-NA and 4-NA with different concentrations of 2-NA (0.6~200 μg·mL^{-1}) in PBS (0.1 M, pH 7.0) at a scan rate of 100 mV s^{-1}. (B) DPV of β-CDs-GQDs/GCE in the presence of 100 μg·mL^{-1} 2-NA and 3-NA with different concentrations of 4-NA (0.6~200 μg·mL^{-1}) in PBS (0.1 M, pH 7.0) at a scan rate of 100 mV s^{-1}. (C) DPV of β-CDs-GQDs/GCE in the presence of 100 μg·mL^{-1} 2-NA and 4-NA with different concentrations of 3-NA (0.6~200 μg·mL^{-1}) in PBS (0.1 M, pH 7.0) at a scan rate of 100 mV·s^{-1}

The comparison for simultaneous separation and detection of nitroaniline isomers between the modified electrodes of the β-CDs-GQDs and nanomaterials is shown in Table 1. It is clear that the β-CDs-GQDs composites modified electrode was better than that displayed references [27-31] for the limit of detection and width of the linearity range. Kokot et al and Chen's group had developed the similar work by DHCBAQS/graphene–nafion and ITO/SAM/AgNPs/β-CD modified electrodes, it can be seen that the linearity ranges were relatively narrow, and the detection limitations of 2-NA and 4-NA were higher than our work. On the other hand, from many relevant references, it is clear that although amount of modified electrode or materials have been used for the nitroaniline recognition reagents, the few reports on their simultaneous detection. More modified electrodes only investigated the 4-NA, such as Ag/CPE [32], metallic silver electrode [33], CS@Ag/CPE [34]. It maybe because 4-NA was largely used as an intermediate or precursor in the manufacture of various industrial and high-volume chemicals including pesticides. In fact, nitroaniline isomers have been listed in priority pollutants in many countries, account for their highly toxic nature and their suspected carcinogenic properties. It is an urgent task to determinate simultaneously. However, even if only 4NA is detected, the sensitivity of our modified electrode is higher than that of 4-NA alone.

Therefore, in conclusion the modified electrode was a good sensor for detection simultaneous of nitroaniline isomers. The results can be explained that β-CDs could form an inclusion complex with GQDs, the β-CDs-GQDs/GCE have been proved to be suitable for stereoselective discriminations.

Table 1. Performances comparison of β-CDs-GQD/GCE for three nitroaniline isomers detection with other electrodes.

Electrode material	*Detection limit (μg•mL^{-1})*			*Linear range (μg•mL^{-1})*			*References*
	2-NA	3-NA	4-NA	2-NA	3-NA	4-NA	
Ag/CPE			0.0058			0.05-100	32
Metallic silver electrode			0.065			0.1-100	33
CS@Ag/CPE			1.19			0.7-140	34
ITO/SAM/AgNPs/β-CD	0.035	0.020	0.014	0.01-100	0.01-100	0.01-100	12
poly-DHCBAQS/graphene–nafion	0.025	0.021	0.019	0.05-0.55	0.05-0.60	0.05-0.60	13
β-CD-GQDs/GCE	0.0066	0.1005	0.0019	0.06-200	0.06-200	0.06-200	This work

In addition, the sensitivity, selectivity, repeatability and stability of electrochemical sensors are important indicators for evaluating its applications. Measuring the responses in 0.5 M PBS (pH=7.0) containing 20 μg·mL^{-1} 2-NA, 3-NA and 4-NA for six to evaluate the repeatability of β-CD-GQDs/GCE. The relative standard deviation (RSD) of 2-NA, 3-NA and 4-NA were 1.4%, 2.1% and 0.9%, respectively. Six different electrodes were prepared under the same conditions to estimate the reproducibility. The RSD of 2-NA, 3-NA and 4-NA was 3.6%, 3.0% and 2.5%, respectively. In addition, the stability of β-CD-GQDs/GCE was also observed. After 10 days, only a slight decrease of the oxidation peak current was observed with the signal change of 3.1% for 2-NA, 4.6% for 3-NA and 3.2% for 4-NA, which indicated that the proposed sensor had appreciable reproducibility and good stability.

3.5. Analysis of practical sample

The β-CDs-GQDs/GCE was used to determine the amount of nitroaniline isomers present in two real sample bought from the local market. The two real samples are carbendazims and trifluralin, which are pesticide and herbicide, respectively. The principal components of the two real sample are nitro-substituted derivatives of aromatic amines and low toxicity. The samples were dissolved in 200 mL distilled water, stirred for 5 min and then the solution was filtered through a funnel to remove the filler and other loading agents and collected in a volumetric flask. DPV measurements were carried out by drawing out 1.0 mL from the above solution and dropping them into 4.0 mL of PBS (pH 7). Then, the three nitroaniline isomers (6.0 μg·mL^{-1}) were added to the above solution to record the voltammograms. None of 3-NA were detected in the analyzed real samples, 2-NA was detected in two real samples and 4-NA was only detected in trifluralin. The analytical results are provided in Table 2. The recoveries, calculated from the standard-addition results, were in the range from 89.2 to 109%.

Table 2. Simultaneous determination of three nitroaniline isomers (concentration in μg·mL^{-1}) in two real sample (n = 3).

Samples	*Detected*（*μg•mL^{-1}*）			*Spiked*（*μg•mL^{-1}*）			*Found*（*μg•mL^{-1}*）			*Recovery*（*%*）		
	2-NA	3-NA	4-NA	2-NA	3-NA	4-NA	2-NA	3-NA	4-NA	2-NA	3-NA	4-NA
Carbendazol	0.66	-	-	6.50	6.50	6.50	7.11	6.64	6.76	99	102	104
Trifluralin	4.83	-	9.02	6.50	6.50	6.50	11.54	6.39	16.23	103	98	111

4. CONCLUSION

In summary, an electrochemical sensor for determination and identification of three nitroaniline isomers was presented in this work. Due to the nanometer effect of GQDs and the specific recognition of β-CDs for nitroaniline isomers, the β-CDs-GQDs/GCE showed a high sensitive and good selective platform for determination and discrimination the nitroaniline isomers. This proposed method has the advantages of high sensitivity, good selectivity, low detection limit and wide detection range, therefore, it has important application value in the detection of nitroaniline isomer pollutants in environmental and biological samples.

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COMPLIANCE WITH ETHICAL STANDARDS

DISCLAIMER
All authors are aware of and accept responsibility for this manuscript.

CONFLICT OF INTEREST
The authors declare that the manuscript has no competing interests.

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