

Detection of di(2-ethylhexyl)phthalate through graphene- β -cyclodextrin composites by electrochemical impedance spectroscopy

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A β -cyclodextrin-graphene (β -CD-G) hybrid composite modified glassy carbon electrode for the first time was used for electrochemically detecting di(2-ethylhexyl)phthalate (DEHP), based on the inclusion of DEHP into β -CD. The electrode was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. At the composites electrode, the impedance value increased linearly with the increasing DEHP concentration in the range of 2 μ M to 18 μ M, the limit of detection was 0.12 μ M (3 σ method), with a correlation coefficient of 0.998. The electrode showed good selectivity, reproducibility and stability. Obviously, the collected amounts of DEHP by β -CD-G could be detected through this electrochemical method. Furthermore, this simple and low-cost sensing platform can in principle be extended to the detection of other phthalate esters which can form host-guest complexes with cyclodextrin.

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1. Introduction

Phthalate esters (PEs) are well-known contaminants in water, soil and the atmosphere, they are used mainly as additives in plastics to impart flexibility, and subsequently can diffuse into the environment during manufacturing, product use and product disposal. Exposure to some PEs may result in carcinogenic and teratogenic effects. Furthermore, some PEs show endocrine effects, *e.g.*, they may act as xenoestrogens.¹⁻⁴ The U.S. Environmental Protection Agency has classified PEs as priority pollutants. Thus, it is rather important to find methods for determination of PEs.

PEs are usually detected by means of chromatographic techniques,⁵ however, a pre-treatment of ultrasonic extraction,⁶ microwave-assisted extraction,⁷ liquid-phase micro extraction,^{8,9} or solid-phase micro extraction,^{10,11} *etc.* is involved. Therefore, this detection method for PEs requires complicated sample preparation processes, expensive instrumentation and is usually time-consuming. It is important to search for a rapid, sensitive, low-cost and simple method to detect PEs. Electrochemical methods compared with those methods offer several advantages including low cost, easy-use, simplicity and the possibility of in-field applications. Especially, electrochemical impedance

spectroscopy (EIS)¹² is a powerful nondestructive method for investigating the boundaries between materials with different types of conductivities and is usually used to probe the interfaces between electronically conducting solid electrodes and ionically conducting electrolytes, where both electrode and electrolyte could be either liquid or solid.¹³ Thus, EIS could be a low-cost and potential approach for the detection of PEs.

Among various different PEs, di-(2-ethylhexyl)phthalate (DEHP), also known as bis-(2-ethylhexyl)phthalate, has caused the most serious pollution. DEHP, a mostly used plasticizer, has been widely used in artificial leather, electric cable covering, toys, medical devices such as intravenous tubing and bags, catheters, nasogastric tubes, dialysis bags and tubing, blood bags and transfusion tubing, and air tubes, *etc.*¹⁴ The annual global production of DEHP has been estimated at 1–20 $\times 10^6$ tons, the potential toxicity of DEHP and its metabolites have caused great alarm, especially for high-risk groups such as children and patients requiring extensive infusions, high hydrophobicity of DEHP makes it highly persistent and bio-accumulating.^{1,15,16} Therefore, the determination of DEHP is attracting more and more attention. Although DEHP molecules are insulated, if they can be preconcentrated on the surface of electrode, the detection of them can be carried out based on the surface characteristic changes of the electrode which can be measured through EIS. Therefore, in this study we decided to detect DEHP by EIS measurement. However, it is necessary to find a suitable electrode material to selectively collect DEHP.

β -cyclodextrin, a molecule with a hydrophilic exterior and hydrophobic cavity, is an oligosaccharide composed of six, seven, or eight glucose units and able to form host-guest complexes with small molecules of the appropriate size and

^aKey Laboratory of Ion Beam Bioengineering, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, People's Republic of China. E-mail: zyw@ipp.ac.cn

^bSchool of Life Sciences, Anhui Agricultural University, Hefei 230036, People's Republic of China. E-mail: xinzhang@ahau.edu.cn; Fax: +86-551-65591413; Tel: +86-551-65595012; +86-551-65786021

[†] Co-first authors.

polarity by noncovalent interactions. Therefore, β -CD has excellent ability in the preconcentration of organic pollutants by forming inclusion complexes.^{17–19} DEHP molecule is supposed to be enclosed in the cavity of β -CD molecule due to hydrophobicity and similar size, and the aromatic ring of DEHP molecules in the cavity could produce maximal contact with the hydrophobic cavity.²⁰ Obviously, β -CD is suitable to selectively collect DEHP for EIS detection. In addition, as is well known, graphene (G) can improve the electrode conductivity, facilitate electron transfer,²¹ and has great surface area. Thus, in this work, β -CD-G composites were synthesized to modify glassy carbon electrode (GCE), which could construct a sensing surface on electrode and be used to carry out the adsorption of DEHP. Furthermore, β -CD molecules were located on the large surface of graphene,^{22,23} which can easily capture plenty of guest DEHP molecules by the cavities of β -CD hosts. The formed inclusion complexes (DEHP and β -CD cavity) block the access of the redox probe to reach the surface of GCE in $K_3Fe(CN)_6$ solution, different concentrations of DEHP included into β -CD-G composites produce different impedance values, thus, the determination of DEHP could be accomplished. In addition, the β -CD-G complex with DEHP is characterized by ultraviolet-visible (UV-vis) spectra. The characteristics of β -CD-G composites electrodes are shown by means of cyclic voltammogram (CV) and EIS. The aim of this study is to develop an analytical method for determining the corresponding phthalate in solution using electrochemical techniques.

2. Experimental

2.1. Reagents and apparatus

Graphite was purchased from Alfa Aesar (Tianjing, China) and DEHP was received from Aladdin Chemistry Co. Ltd (Shanghai, China). β -cyclodextrin, hydrazine solution (50 wt%) and ammonia solution (25 wt%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Unless otherwise stated, other reagents were of analytical grade. All aqueous solutions were prepared with deionized water from a Milli-Q Plus system (Millipore, China).

Fourier transform-infrared (FT-IR) spectra were recorded in a FT-IR spectrometer (Alpha-T, Bruker). A pH meter (Mettler Toledo FE20, Switzerland) was used for measuring pH. UV-vis spectra were obtained by a UV-2550 spectrophotometer (Shimadzu, Japan).

Electrochemical experiments were performed using a CHI 660D computer-controlled electrochemical workstation (CH Instruments, USA) with a standard three-electrode system. A bare GCE (diameter of 3 mm) or modified GCE served as a working electrode; a platinum wire was used as a counter-electrode with a saturated Ag/AgCl electrode completing the cell assembly.

2.2. Synthesis of pure graphene oxide and β -CD-graphene hybrid composites

Graphene oxide (GO) was synthesized from graphite powder by Hummers and Offeman method.²⁴ β -CD-graphene (β -CD-G)

hybrid composites were synthesized as previously described.²³ Briefly, in a separate vial, 160 mg β -CD was dissolved in 40 mL GO (0.1 mg mL^{-1}) aqueous solution and continuously stirred for half an hour, followed by addition of 15 μL hydrazine solution drop by drop, next, the mixed solution was heated at 80°C for 2 h with constant stirring obtaining a black solution. The black solution was treated by filtration and centrifugation, and then dried at 60°C under vacuum to obtain β -CD-G composites. Pure graphene was obtained from the reduction of GO through the procedure previously reported.²³

2.3. UV-vis measurements of β -CD-GO and β -CD-G solutions

2 mg GO nanosheets were dispersed in 20 mL β -CD aqueous solution (4 mg mL^{-1}) by ultrasonication for half an hour, and β -CD-GO composites solution was formed for the measurement of UV-vis spectra. 2 mg synthesized β -CD-G composites were also dissolved in 20 mL water for measurement of UV-vis spectra.

2.4. Preparation of modified electrode

Prior to modification, a bare GCE was polished to be mirror-like with 1, 0.3 and $0.05 \mu\text{m}$ alumina slurry, rinsed thoroughly with deionized water between each polishing step, then sonicated successively with 1 : 1 nitric acid, ethanol, and deionized water, respectively, for 4 min in an ultrasonic bath and dried in nitrogen.

Then 10 mg β -CD-G composites was dispersed in 10 mL ethanol under ultrasound for 30 min, and 5 μL aliquot of this dispersion solution was dropped onto the surface of the cleaned GCE and dried in air at room temperature. Thus, the modified electrodes were obtained.

2.5. Electrochemical measurements

The CV experiments were performed in 2 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl solution with the scan rate of 100 mV s^{-1} . The EIS experiments were performed in the presence of a degassed phosphate buffer solution (PBS(0.1 M), pH 7.0) containing 2 mM $K_3Fe(CN)_6$ and 0.1 M KCl, the frequency range was 0.1–100 kHz with a signal amplitude of 5 mV. The solutions of DEHP and other interference test samples were prepared with ethanol. The as-prepared β -CD-G electrodes were dipped into DEHP solution for 2 h with stirring at room temperature in order to collect DEHP, and then carefully washed using ethanol solution. The electrolyte solutions were deoxygenated with nitrogen bubbling for 20 min before each voltammetric run, and all electrochemical experiments were performed at room temperature and under nitrogen atmosphere.

3. Results and discussion

The experimental procedure is schematically shown in Scheme 1. The β -CD-G composites were synthesized, and then used to modify the electrode. After preconcentration of DEHP through the composite materials, an inclusion complex of β -CD and DEHP blocking the electron transfer of redox probe was

formed, and a corresponding impedance value could be obtained, thus, DEHP could be detected.

3.1. UV-vis spectra of β -CD-GO and β -CD-G composites solution

The UV-vis spectra of β -CD-GO and β -CD-G composites solutions are observed in Fig. 1. As can be seen, a UV absorption band appeared at about 232 nm corresponding to the $\pi \rightarrow \pi^*$ transition of aromatic C=C bonds, which was the typical UV-vis absorption peak of GO of β -CD-GO composites.²⁵ After reduction in the presence of hydrazine, the maximum absorption peak at about 276 nm showed characterization of G of β -CD-G composites. The 44 nm shift of the adsorption peak from 232 to 276 nm suggested that the β -CD-GO were successfully reduced to β -CD-G.²⁶

3.2. FT-IR spectra of G, β -CD, and β -CD-G composites

FT-IR spectra of G, β -CD, and β -CD-G materials are shown in Fig. 2. It was found that the FT-IR spectrum of G showed an absorption band at 1575 cm^{-1} , which is related to the C=C group. The FT-IR spectra of β -CD-G composites show typical β -CD absorption features of the ring vibrations at 577, 709, 758, and 945 cm^{-1} , and O-H stretching vibrations are shown at around 3500 cm^{-1} . All these clearly show that β -CD-G materials were synthesized and β -CD molecules were located on the surface of G.^{23,27}

3.3. UV-vis characterizations of DEHP solution preconcentrated by β -CD molecules and β -CD-G composites

In order to study the preconcentration of DEHP into the cavities of β -CD molecules and β -CD-G composites, the UV-vis characterizations of DEHP solutions adsorbed by different samples were measured and are shown in Fig. 3. At first, 20 mg DEHP was dissolved in 6 mL ethanol solution obtaining the standard solution of DEHP. Then, 0.1 mL of such solution was added into 3 mL ethanol. The UV characterization of the solution was measured at

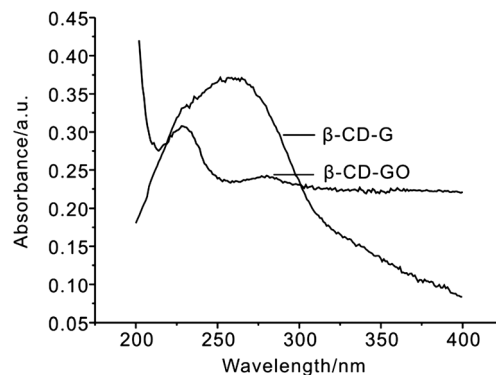
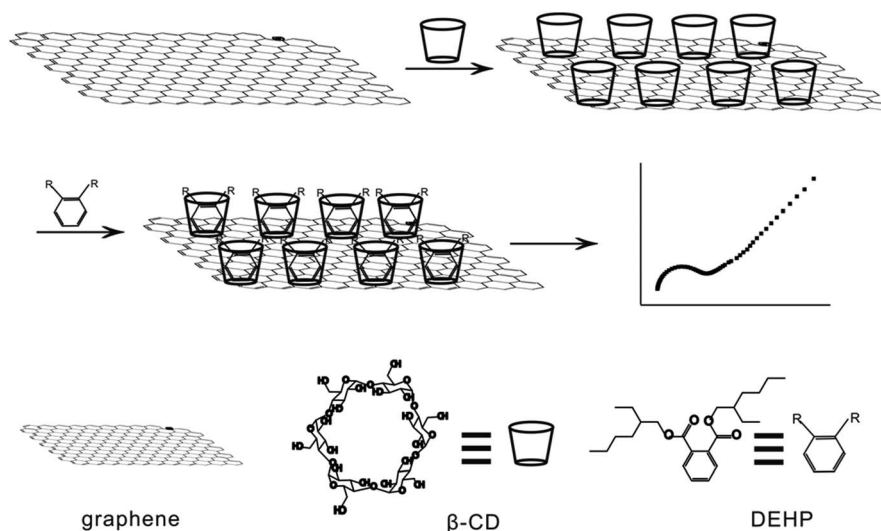


Fig. 1 UV-vis absorption spectra of β -CD-GO and β -CD-G composites.

272 nm,²⁵ and the intensity was 0.516 a.u. as shown in Fig. 3. Under the same conditions, 16 mg β -CD or β -CD-G composites were added into DEHP standard solution (6 mL) by shaking for 24 h at room temperature. After centrifugation and filtration, 0.1 mL resulted solution was added into 3 mL ethanol. Fig. 3 shows that the intensities of adsorption peak were 0.368 a.u. and 0.332 a.u., respectively. It is evident that the intensities decreased compared with standard solution, which indicated that DEHP could be collected by β -CD or β -CD-G composites. In addition, the adsorption intensity of solution treated by β -CD-G composites was the least, that is to say, the amount of DEHP binding with β -CD-G composites was larger than that binding with β -CD under the same conditions, which might be due to abundant and orderly β -CD molecules located on the large surface of G²³ increasing the contract area with DEHP. Thus, β -CD-G composites were chosen to modify electrodes for detection of DEHP.

3.4. Electrochemical characterization of β -CD-G composites electrode

The electrochemical properties of bare GC electrode and modified electrode were characterized by CVs and EIS in 2 mM



Scheme 1 Procedure of synthesizing β -CD-G composites and detecting DEHP.

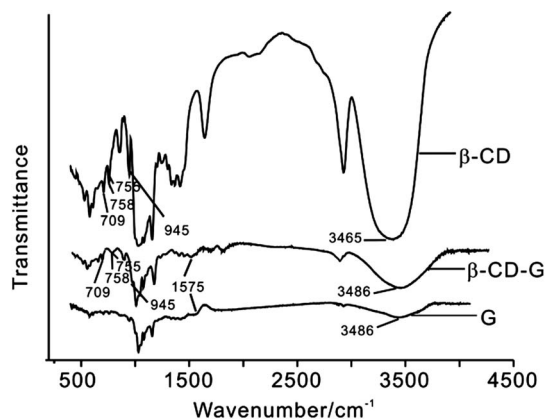


Fig. 2 FT-IR spectra of G, β -CD and β -CD-G composites.

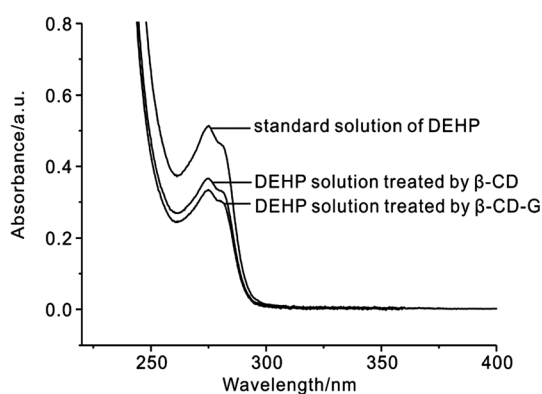


Fig. 3 UV-vis absorption spectra of standard DEHP solution, and DEHP solution treated by β -CD or β -CD-G composites.

$\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCl solution. In Fig. 4(a), the CV of bare GCE shows a quasi-reversible redox reaction. However, it could be found that the amperometric response of the redox probe decreased and the peak-to-peak separation increased at the

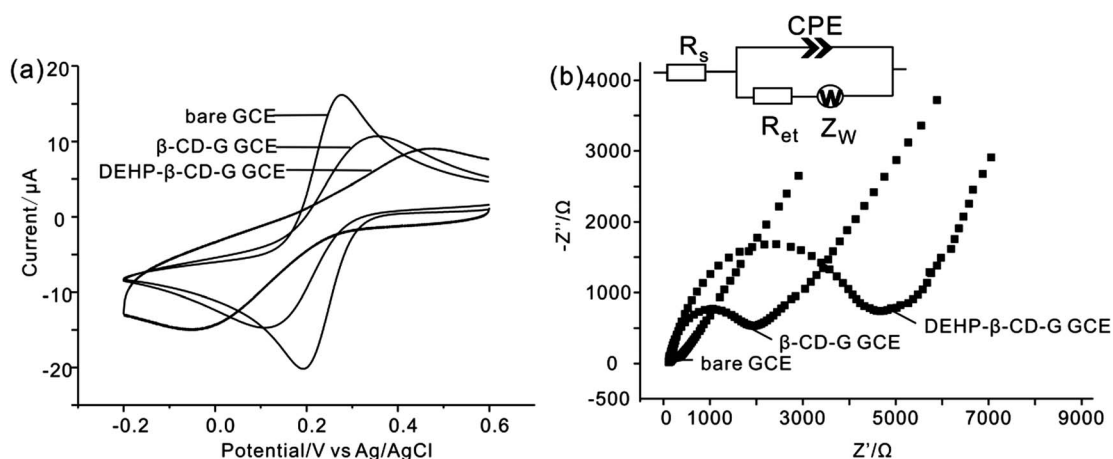


Fig. 4 CVs (a) and EIS plots (b) of bare GCE, β -CD-G/GCE and DEHP- β -CD-G/GCE in the solution containing 2 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ and 0.1 M KCl. Inset: Randle's equivalent circuit corresponding to the impedance features.

Table 1 Influence of ratio of GO to β -CD on the EIS of the sensor in the presence of 4 μM DEHP

Ratio (GO : β -CD)	ΔR_{et} (Ω)
1 : 20	900
1 : 30	1000
1 : 40	1800
1 : 50	1550
1 : 60	1400

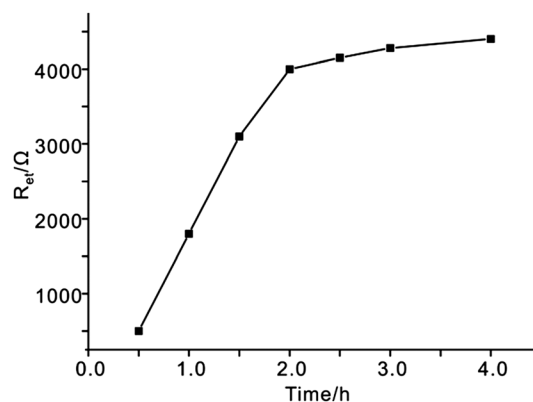


Fig. 5 The effect of preconcentration time on electron-transfer resistance (R_{et}) at the DEHP- β -CD-G/GCE.

β -CD-G composites electrode and the electrode with pre-concentrated DEHP (3 μM), respectively. Clearly, the electron-transfer was blocked at β -CD-G modified GCE compared to bare GCE, due to attachment of the β -CD-G composites on the surface of electrode. After β -CD-G electrode preconcentrated with DEHP, the electron-transfer between $\text{Fe}(\text{CN})_6^{3-/4-}$ and the electrode surface was further inhibited because the insulated DEHP blocked further the diffusion of the redox probe.

In order to understand deeply the characterization of the modified electrode, further investigation was performed by EIS

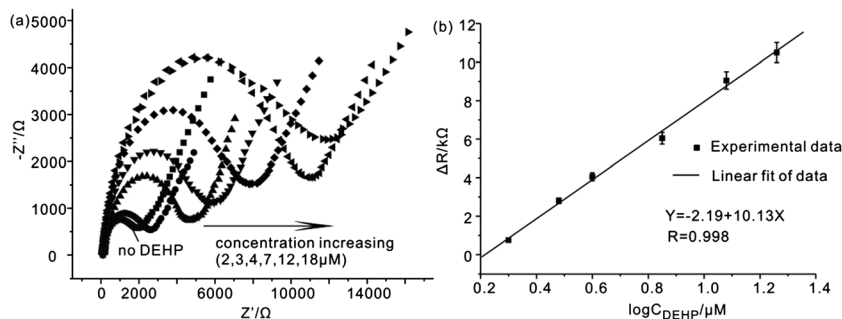


Fig. 6 (a) Nyquist diagram of EIS of a β -CD-G CE before and after immersing in DEHP solutions with different concentrations (2, 3, 4, 7, 12 and 18 μM). (b) Plots of R_{et} as a function of logarithmic values of DEHP concentrations. The standard error in each concentration was obtained by measurements of three samples.

measurement, which could provide information on the electrode surface based on the change of impedance value. The impedance spectra of different electrodes were compared in Fig. 4(b). The impedance value of bare GCE was the least (80 Ω) owing to almost no barrier on the surface of bare GCE. The impedance value of β -CD-G composites electrode with DEHP was 4840 Ω and larger than that of β -CD-G electrode (2000 Ω). Obviously, the inclusion of non-conductor DEHP into the cavity of β -CD could increase the impedance value to some degree, which indicated that detection of DEHP could be carried out by EIS measurement. These results are supported by the above cyclic voltammetric responses. Inset of Fig. 4(b) shows a typical equivalent circuit for the physical model of an electrochemical interface. The impedance data were fitted with commercial software Zview2. Cdl was the interfacial double layer capacitance between an electrode and a solution. In this experiment, the surface area of β -CD-G electrode was large, and the impedance of solid electrode deviated from the purely capacitive behavior, so constant phase element (CPE) was used to fit the impedance data because CPE was closely related to the insulating property of the electrode/electrolyte interface. R_{et} corresponds to the interfacial electron-transfer resistance for the redox probe. As can also be seen in Fig. 4(b), the changes in R_{et} were much larger than those in other impedance elements, therefore, R_{et} was considered as a suitable signal for expressing the interfacial properties of the prepared sensor during pre-concentration procedures. R_s is the ohmic resistance of the electrolyte solution. Z_w is the Warburg impedance, resulting from the diffusion of ions from the bulk electrolyte to the electrode interface.²⁸

Table 3 Molecular volumes and impedance values (ΔR_{et}) of the seven interferences

Interferents (μM)	Molecular volume (\AA)	ΔR_{et} (Ω)
trichloroethene (40)	155	60
TeCB (40)	137	50
chlorobenzene (40)	180	60
anthracene (10)	315	70
cypermethrin (10)	313	50
acetofenatate (10)	217	460
DDT (10)	508	40

Table 4 Determination of DEHP in contaminated sample solutions

	Found (μM)	Added (μM)	After added (μM)	Mean recovery (%)
Sample 1	0.18	4.0	4.24	101.4
Sample 2	0.5	8.0	8.42	99.1

3.5. Effect of ratio of GO to β -CD

The different ratio of GO and β -CD could cause great influence for synthesized β -CD-G composites to preconcentrate DEHP (4 μM). Table 1 shows the difference values of electron-transfer resistance (ΔR_{et}) of several ratios (GO : β -CD). When the ratio of GO and β -CD reached to 1 : 40, the ΔR_{et} value was the biggest ($\sim 1800 \Omega$). Consequently, this ratio (1 : 40) was utilized for further experiments.

Table 2 Comparison of the performances of various detection methods for DEHP

Methods	Linear range (nM)	Detection temperature ($^{\circ}\text{C}$)	Detection limit (nM)	Reference
GC	25.6–128	200–300	—	5
GC-MS	560–1900	280–300	—	6
GC-MS	128–256 000	200–300	56.4	7
GC	256–128 000	260–300	—	8
GC-MS	25.6–0.256	260–300	0.0256	9
GC-MS	0–23 100	220–270	8.1	10
GC-MS	256–25 640	250–280	8.2	11
EIS	2000–18 000	Room temperature	120	This method

3.6. Effect of preconcentration time

A preconcentration step was able to assure the capture of DEHP molecules by the β -CD-G prior to EIS measurements. The preconcentration time was investigated from 0.5 to 5 h. As shown in Fig. 5, the electron-transfer resistance value increased quickly initially, and reached a plateau when time was up to 2 h. Thus, 2 h was chosen as the optimal preconcentration time in the following experiments.

3.7. EIS measurements with different concentration of DEHP

According to the above mentioned optimised conditions, 5 μ L β -CD-G composites solution was dropped on the surface of electrode and dried under N_2 atmosphere, then the electrode was immersed for 2 h in DEHP solution with different concentration. The different impedance spectra of the electrode were obtained in pH 7.0 PBS containing 2 mM $K_3Fe(CN)_6$ and 0.1 M KCl as shown in Fig. 6(a). The impedance value increased gradually with the increasing DEHP concentration ranging from 2 μ M to 18 μ M. Fig. 6(b) depicts a linear relation of ΔR_{et} vs. $\log C_{DEHP}$, where C_{DEHP} is the concentration of DEHP, with a correlation coefficient of 0.998. The linear equation is:

$$\Delta R_{et} (\Omega) = -2.19 + 10.13 \log C_{DEHP} (\mu M)$$

In the equation, ΔR_{et} can be evaluated as follows:

$$\Delta R_{et} = R_{et} (\text{DEHP-}\beta\text{-CD-G}) - R_{et} (\beta\text{-CD-G})$$

where R_{et} (DEHP- β -CD-G) is the electron-transfer impedance of β -CD-G composites adsorbed with DEHP, and R_{et} (β -CD-G) is the one without adsorption of DEHP. From the results mentioned above, the β -CD-G composites electrode could be used to detect DEHP by EIS measurement.

A comparison of linear range, detection temperature and detection limit for the β -CD-G modified electrode with other DEHP detection methods in the literature is shown in Table 2. As can be seen, this electrochemical method is low-cost and simple in comparison with previous methods. Therefore, the G- β -CD electrode could be used for the preparation of an impedance sensor for the detection of DEHP with convenience under room temperature.

3.8. Interference

The effect of interferents on the β -CD-G sensor was investigated. Seven organic pollutants with different sizes (namely trichloroethene, 1,2,3,4-tetrachlorobenzene (TeCB), chlorobenzene, anthracene, DDT, acetofenate and cypermethrin) were chosen as the interferents, which were usually found in contaminated water. Table 3 depicts the impedance values of interferents, it could be seen that the impedance values of the pollutants were all small and might be omitted, compared with the value of DEHP ($\Delta R_{et} = 2000 \Omega$). That is to say, the interferents had no obvious interference on the detection of DEHP, which may be related with the volume and

hydrophobicity or hydrophilicity of the molecule. The volume of β -CD cavity is 262 \AA^3 and the cavity is hydrophobic,²⁹ and the molecular volumes of the seven interferents are shown in Table 3. It can be seen that anthracene, DDT, and cypermethrin show big molecular volumes ($>262 \text{\AA}^3$), so that it is hard for them to enter the cavity of β -CD. The molecular volumes of trichloroethene, TeCB, and chlorobenzene are small ($<262 \text{\AA}^3$), but these molecules are hydrophilic and not easy to stay in the cavity of β -CD. However, acetofenate shows slight interference in the determination of DEHP, which might be because of its hydrophobic property and volume almost close to that of β -CD cavity.

3.9. Reproducibility and stability of the composites electrode

The relative standard deviation (RSD) was 3.9% for the composites electrode ($n = 5$), which shows an acceptable reproducibility. After the β -CD-G composites electrode was stored in a refrigerator at 4 $^\circ\text{C}$ for 10 days, only a small decrease of the R_{et} was observed with a signal change of 4.5%, which indicated the excellent stability of β -CD-G composites fixed on the surface of GCE.

3.10. Analytical applicability

To investigate the application of the sensor in practical analysis, the β -CD-G composites electrode was used to determine the concentration of DEHP in wastewater samples collected from a plastics factory. The wastewater was treated and extracted with ethanol, and then the samples were diluted 10 times with ethanol. Using a standard addition method, the recoveries of DEHP samples with concentrations of 4.0 μ M (sample 1) and 8.0 μ M (sample 2) were obtained as shown in Table 4. The results show that this composites electrode might have a potential use for detection of DEHP.

4. Conclusions

In this work, we developed an electrochemical impedance sensor for determination of DEHP, based on the high host-guest recognition and enrichment capability of β -CD-G. The DEHP could be included into cyclodextrin cavity of β -CD-G to form the inclusion complex, which was proven by UV-vis spectra, and detected by EIS measurement. The results show a linear relationship between impedance values and concentrations of DEHP and also demonstrated fine reproducibility and stability of the sensor. This study may contribute to the application of graphene composite materials in detection of PEs.

Acknowledgements

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