

Amino β -cyclodextrin-functionalized GS/MWCNTs for Simultaneous Electrochemical Determination of *p*-aminophenol and Acetaminophen

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In this study, a rapid and sensitive electrochemical sensor based on amino β -cyclodextrins (NH₂- β -CD) functionalized graphene and multi-walled carbon nanotubes (MWCNTs) nanohybrids was successfully constructed for the simultaneous determination of *p*-aminophenol (*p*-AP) and acetaminophen (AC). Graphene and MWCNTs were oxidized with strong acid to give carboxyl groups (COOH-f-GS/MWCNTs). Then, the NH₂- β -CD was immobilized on its surface by EDC and NHS to prepare a porous hybrid nanocomposite (β -CD-NHCO-f-GS/MWCNTs). The composite material displays a well synergistic effect of high electrocatalytic activity and excellent conductivity of COOH-f-GS/MWCNTs and high supramolecular recognition capability of NH₂- β -CD. The electrocatalytic mechanism and catalytic process are discussed. Under the optimum conditions, the detection limits of the as-prepared electrochemical sensor are 0.11 mM and 0.15 mM for *p*-AP and AC, respectively. The linear ranges are 1.0 mM to 1.32 mM for *p*-AP and 0.6 mM to 0.44 mM for AC. More importantly, this result was measured in the presence of each other. The electrochemical sensor can simultaneously display obvious and accurate response to *p*-AP and AC at different potentials with high sensitivity and less interferences.

Keywords: Amino β -cyclodextrins; Graphene; Multi-walled carbon nanotube; *p*-Aminophenol; Acetaminophen

1. INTRODUCTION

Acetaminophen (AC) is an acetanilide antipyretic analgesic also known as paracetamol [1]. It is one of the most commonly used over-the-counter drugs in the world and can be used to treat headache, muscle soreness, arthritis, back pain, toothache, cold, fever and other diseases [2-5]. The recommended dosage of AC has fewer side effects on the human body, but excessive intake can lead to liver and kidney

toxicity [6-8]. *p*-Aminophenol (*p*-AP) is the main hydrolytic intermediate of AC [9]. *p*-AP as a widely used organic chemical intermediate has been used in medicine, rubber, dye preparation, feed, oil and other fields [10-13]. It is possible that a large amount of *p*-AP is released into the environment. Because of its nephrotoxicity and teratogenicity, the maximum content of *p*-AP in drugs is limited to 50 ppm (0.005%, w/w) according to the U.S., European and Chinese Pharmacopoeias [14-16]. Therefore, it is necessary to establish a simple, sensitive and accurate method for the determination of AC and *p*-AP.

Several methods for the simultaneous determination of AC and other phenols have been reported, including high performance liquid chromatography, gas chromatography, titrimetry, spectrophotometry and electrochemical methods [17-21]. Among these methods, electrochemical technology based on chemically modified electrodes has attracted much attention due to its fast response, high selectivity and sensitivity, wide linear range, simple preparation and simple sample pretreatment. However, AC and most other phenols are electroactive and often coexist in real samples. It remains a challenge to overcome the interference between these compounds by constructing electrochemical sensors with high stability, high selectivity and high sensitivity.

Nanoscience and nanotechnology play an important role in the development of modified electrodes. Graphene sheets (GS) are two-dimensional (2D) carbon materials with honeycomb structure composed of carbon atoms [22]. The conductivity of graphene oxide (GO) is not outstanding, but its rich oxygen-containing functional groups (-COOH, -C=O etc.) provide many possibilities for further modification [23]. Multiwalled carbon nanotubes (MWCNTs) are 1D carbon nanomaterials with special structures [24]. They are a type of multilayer coaxial tube composed of hexagonal carbon atoms. Due to its high conductivity, electrocatalytic activity, chemical and physical stability and large specific surface area, MWCNTs have been used in the construction of many high-performance nano electrochemical devices [25-29]. However, due to the intrinsic van der Waals interaction between pristine tubes, MWCNTs bundle together on a large scale and are insoluble in routine solvents, which seriously limits their application. It has been reported that aggressive oxidation and functionalization can be used to resolve this problem [30].

β -cyclodextrins (β -CD) are polymerized by seven pyranose units, which looks like a conical cylinder in the molecular model [31]. The cavity structure of β -CD hosts an electron and hydrophobic internal microenvironment, which enables easy trapping of hydrophobic molecules in the cavity via replacement of water [32]. Based on this host-guest reaction, β -CD has been used to construct many inexpensive but sensitive and selective electrochemical sensors [33-35]. It has been reported that modification of β -CD by several functional groups on the broader rim can enhance the encapsulation ability depending on the characteristics of the guest molecule [36].

Thus, in this study, considering the synergetic effect of the high electrocatalytic activity and conductivity of COOH-f-GS/MWCNTs and the high supramolecular recognition capability of NH₂- β -CD, a sensitive and simple electrochemical method for the simultaneous determination of AC and *p*-AP is established. The β -CD-NHCO-f-GS/MWCNTs nanocomposite is found to exhibit excellent performance.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Apparatus

Multiwalled carbon nanotubes (MWCNTs) and graphene were purchased from Nanjing XFNANO Materials Tech Co. (Nanjing, China). NH_2 - β -cyclodextrins (NH_2 - β -CD) was purchased from Zhiyuan Biotechnology Co. (Shandong, China). N-hydroxysulfosuccinimide (NHS) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) were purchased from Aladdin Chemical Reagents Co. Ltd. (Shanghai, China). All other reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). The water used in the experiment was distilled water.

Electrochemical experiments were carried out on a CHI 660E electrochemical workstation (Chenhua Instruments, Shanghai, China), coupled with a GCE, a platinum wire and a calomel electrode at 298 K. The surface morphologies were observed by a scanning electron microscope (SEM, FEI Inspect F50, USA). The surface elemental composition and the characterization of the various functional groups of the nanocomposite were carried out using X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, Thermo Scientific, USA) and Fourier transform infrared spectrometry (FTIR, Thermo Fisher Scientific, USA).

2.2 Synthesis of COOH-f-GS/MWCNTs

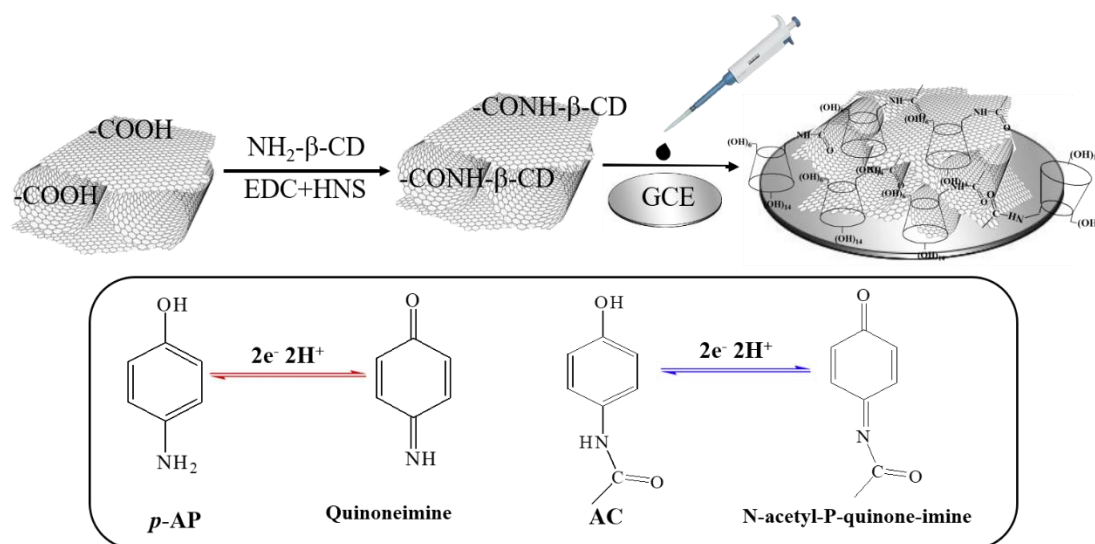
COOH-f-GS/MWCNTs were prepared according to a previously reported method [37]. The pristine GS/MWCNTs were placed in a mixture of sulfuric acid and nitric acid (3:1), ultrasonicated for 2 h, and then heated at 80 °C for 24 h. After cooling to room temperature, the pH value of the suspension was adjusted to a value of 8.0 in an ice bath. After centrifugation and drying, as solid was the product was obtained.

2.3 Synthesis of β -CD-NHCO-f-GS/MWCNTs

Thirty milligrams of COOH-f-GS/MWCNTs was ultrasonicated in 5 mL PBS (0.1 M, pH 7.0) for 30 min. Then 50 mg EDC and 25 mg NHS were added to the solution. After stirring the above solution for 1 h, 30 mg NH_2 - β -CD was added and stirred for 2 h. Finally, the β -CD-NHCO-f-GS/MWCNTs were obtained by centrifugation several times.

2.4 Construction of the modified electrodes

The GCE with a diameter of 3 mm was polished to a mirror surface with 0.05 mm and 0.3 mm alumina powder. Then, 5 mL of a homogeneous suspension of β -CD-NHCO-f-GS/MWCNTs (1 mg/mL) was drop cast onto the bare GCE surface and dried in air (used as β -CD-NHCO-f-GS/MWCNTs/GCE). Other electrodes used for comparison were prepared in the same way. The fabrication process of the modified electrode is shown in Scheme. 1.



Scheme 1. The schematic illustration of the sensor fabrication progress and the mechanism of electrochemical oxidation of AC and *p*-AP.

3. RESULTS AND DISCUSSION

3.1 Characterization of the modified materials

To analyze the morphology of the modified electrodes, SEM (Fig. 1) was employed to study the microstructures of GO, COOH-MWCNTs and $\beta\text{-CD-NHCO-f-GS/MWCNTs}$. GO exhibits a smooth surface and wrinkled form (Fig. 1A), whereas COOH-MWCNTs are entangled with each other (Fig. 1B). The $\beta\text{-CD-NHCO-f-GS/MWCNTs}$ show that MWCNTs are bound to the GO surface, resulting in the formation of a nanochannel (Fig. 1C).

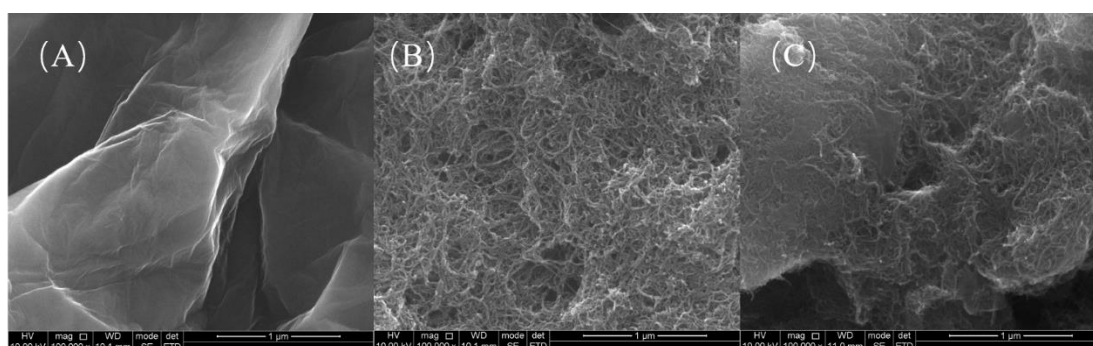


Figure 1. SEM of COOH-GS (A), COOH-MWCNTs (B) and $\beta\text{-CD-NHCO-f-GS/MWCNTs}$ (C).

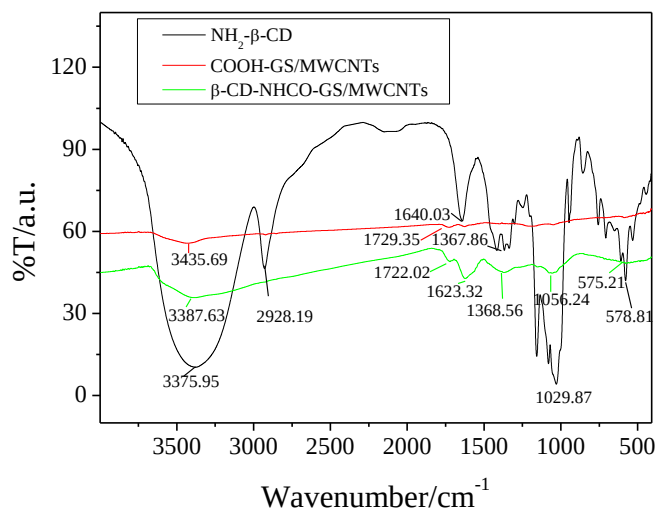


Figure 2. FT-IR spectra of β -CD-NHCO-f-GS/MWCNTs (green), COOH-GS/MWCNTs (red) and NH_2 - β -CD (black).

Figure 2 displays the FTIR spectra for NH_2 - β -CD, COOH-GS/MWCNTs and β -CD-NHCO-f-GS/MWCNTs. A broad peak is observed at approximately 3400 cm^{-1} , which is the characteristic peak due to -OH groups [31]. The peaks observed at 2928 cm^{-1} are attributed to asymmetric and symmetric CH_2 stretching in NH_2 - β -CD [32]. The peaks observed at 578 cm^{-1} and 575 cm^{-1} are the absorption features due to the ring vibrations of NH_2 - β -CD. The FTIR spectra for β -CD-NHCO-f-GS/MWCNTs and NH_2 - β -CD exhibit the strong bands at 1056 and 1029 cm^{-1} , which are attributed to the asymmetric glycosidic vibration of C-O-C and the coupled tensile vibration of the C-C and C-O groups of NH_2 - β -CD. After the addition of EDC and NHS, the carboxylic group of the COOH-GS/MWCNTs reacts with the amino groups of NH_2 - β -CD to form β -CD-NHCO-f-GS/MWCNTs. The C=O bond of -COOH at 1729 cm^{-1} in COOH-GS/MWCNTs is shifted to 1722 cm^{-1} in β -CD-NHCO-f-GS/MWCNTs, which is mainly due to the electronegativity of hydroxyl groups induced by conjugation. The peaks at 1623 , 1367 and 1368 cm^{-1} are attributed to the absorption bands for C-N and C=N stretching vibrations.

Figure 3A shows the XPS spectrum of the C1 s of the NH_2 - β -CD, COOH-GS/MWCNTs and β -CD-NHCO-f-GS/MWCNTs. The XPS full scan survey for the three materials shows that the C 1s and O 1s peaks were located at 285 eV and 537 eV , respectively.

In addition, compared with COOH-GS/MWCNTs, the N1 s peak signal intensity measured for the β -CD-NHCO-f-GS/MWCNTs nanoprobe at 394 eV is increased, which means that NH_2 - β -CD and COOH-GS/MWCNTs are covalently bonded to form β -CD-NHCO-f-GS/MWCNTs. Figure 3B displays three typical characteristic peaks at 283 , 286 and 284.8 eV , corresponding to the C-N, C-C and C-O of NH_2 - β -CD, respectively [38,39]. Figure 3C shows the C1 s spectrum for COOH-GS/MWCNTs. The peaks observed at 284.8 , 286.2 and 290.8 eV are attributed to C-O, C-C and C=O, respectively. Compared with Figure 3C, Figure 3D shows an additional C-N peak at 283 eV . All of these results indicate that β -CD-NHCO-f-GS/MWCNTs were successfully prepared.

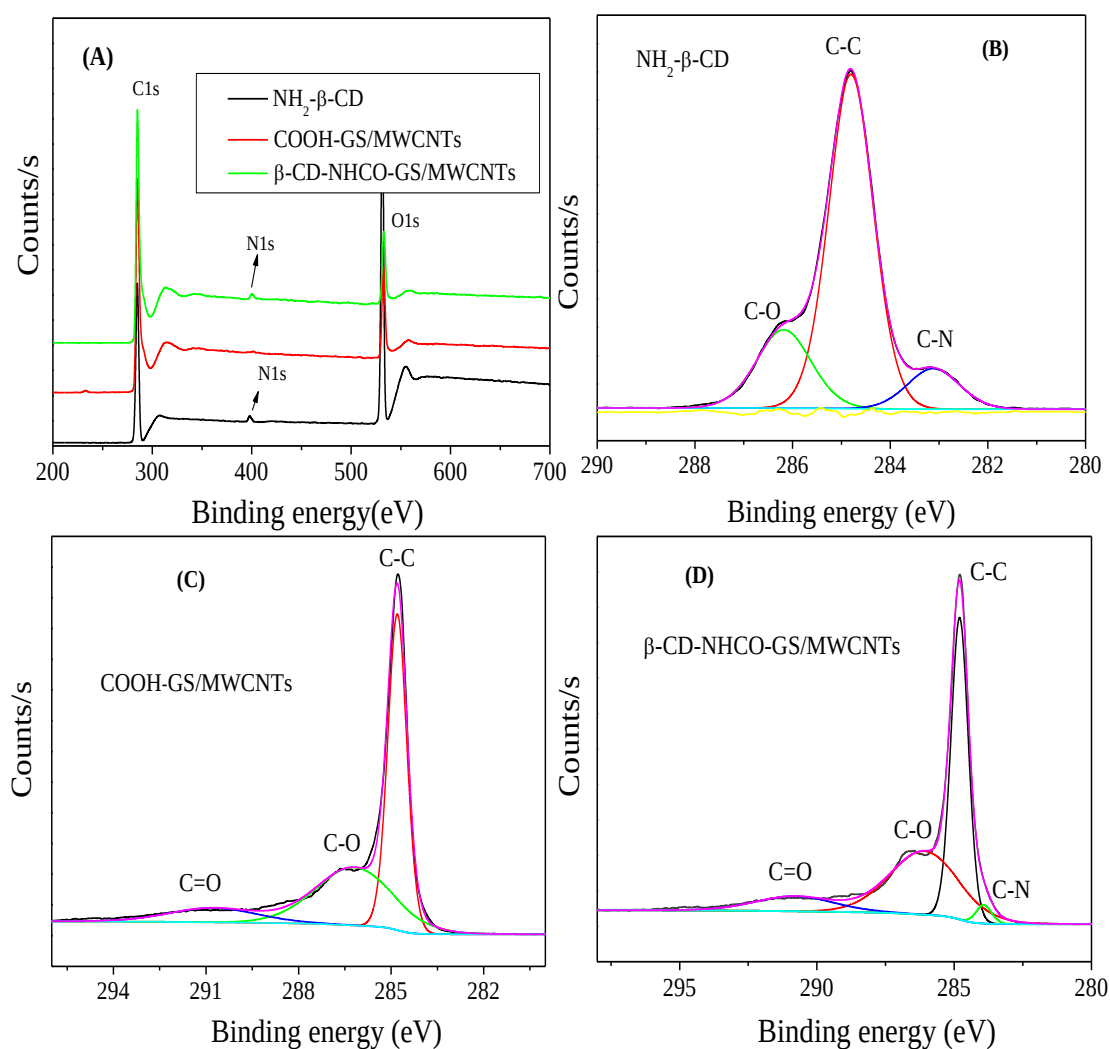


Figure 3. The XPS survey scan (A) and deconvoluted C1 s spectra of NH₂-β-CD (B), COOH-GS/MWCNTs (C) and β-CD-NHCO-f-GS/MWCNTs (D)

3.2 Electrochemical behavior of the modified electrodes

Figure 4A shows the cyclic voltammograms (CVs) for different modified electrodes. The addition of COOH-GS/MWCNTs promotes electronic transmission and improves the conductivity of the modified electrode.

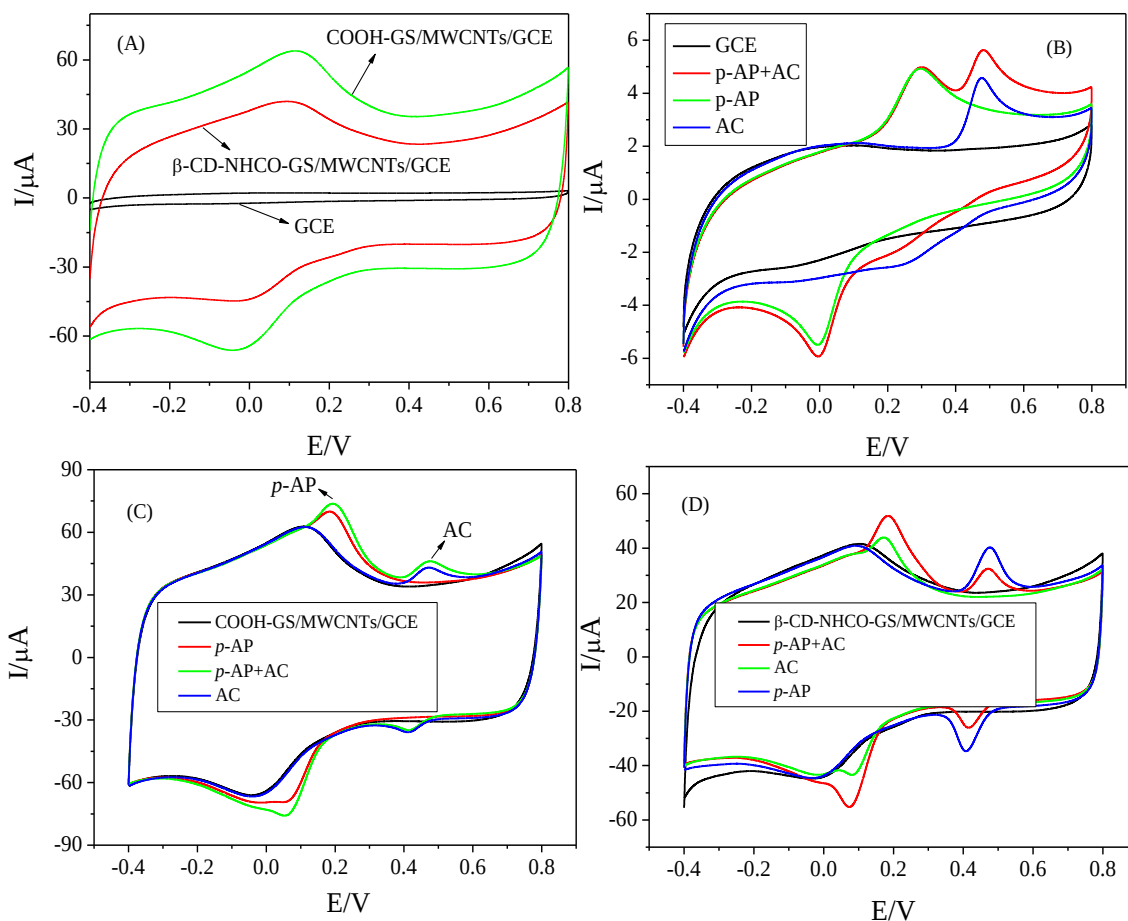


Figure 4. CV curves of different modified electrodes in 0.1 M PBS (pH=6.0) (A), CV curves of 6 mM *p*-AP, 6 mM AC and the mixture of *p*-AP and AC at the bare GCE (B), COOH-GS/MWCNTs/GCE (C) and β -CD-NHCO-f-GS/MWCNTs/GCE (D) in 0.1 M pH 6.0 PBS.

The CVs for the bare GCE (Figure 4B), COOH-GS/MWCNTs/GCE (Figure 4C) and β -CD-NHCO-f-GS/MWCNTs/GCE (Fig. 4D) in the presence of 6 mM *p*-AP, 6 mM AC and the mixture of *p*-AP and AC in 0.1 M PBS (pH 6.0) at a scan rate of 100 mV/s are also investigated. The electrochemical response signals of *p*-AP and AC are observed on all three different modified electrodes, but the separation of peak potentials on the bare electrode is the smallest and there is no obvious reduction peak. Compared with COOH-GS/MWCNTs, β -CD-NHCO-f-GS/MWCNTs has the best electrocatalytic performance for *p*-AP and AC, although its conductivity is not as high as COOH-GS/MWCNTs.

3.3 Effect of pH and scan rate

The effect of pH on the electrochemical response of *p*-AP and AC in PBS was studied by CV technique. Figure 5A shows the CV curves of β -CD-NHCO-f-GS/MWCNTs/GCE in 0.1 M PBS containing 6 mM *p*-AP and 6 mM AC at different pH values. The linear relationship between peak current and pH value is shown in Figure 5B. The peak currents of both *p*-AP and AC increased from pH

3.0 to 6.0 and then decreased. The maximum peak currents of *p*-AP and AC reach at pH 6.0. Therefore, 0.1 M PBS with pH value of 6.0 was selected as the electrolyte base solution for the further experiments.

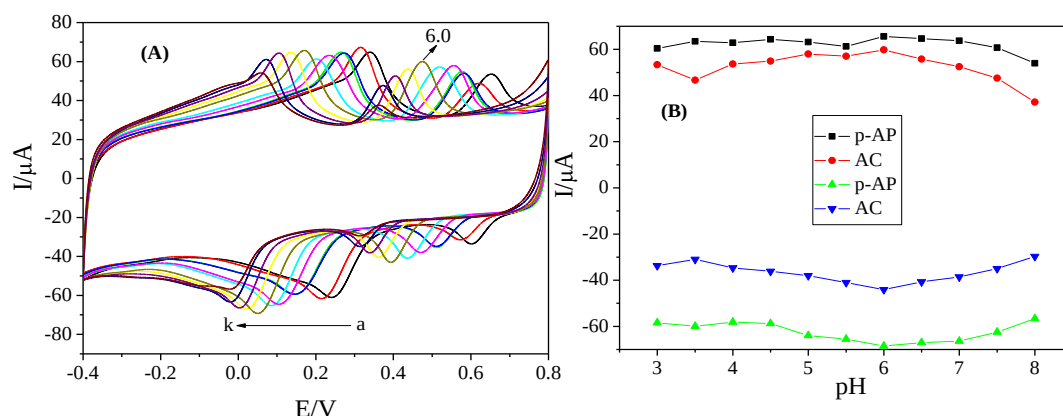


Figure 5. CV curves of β -CD-NHCO-f-GS/MWCNTs/GCE in 0.1 M PBS of different pH containing 6 mM *p*-AP and 6 mM AC (A); The linear relationship between peak currents and pH value (B).

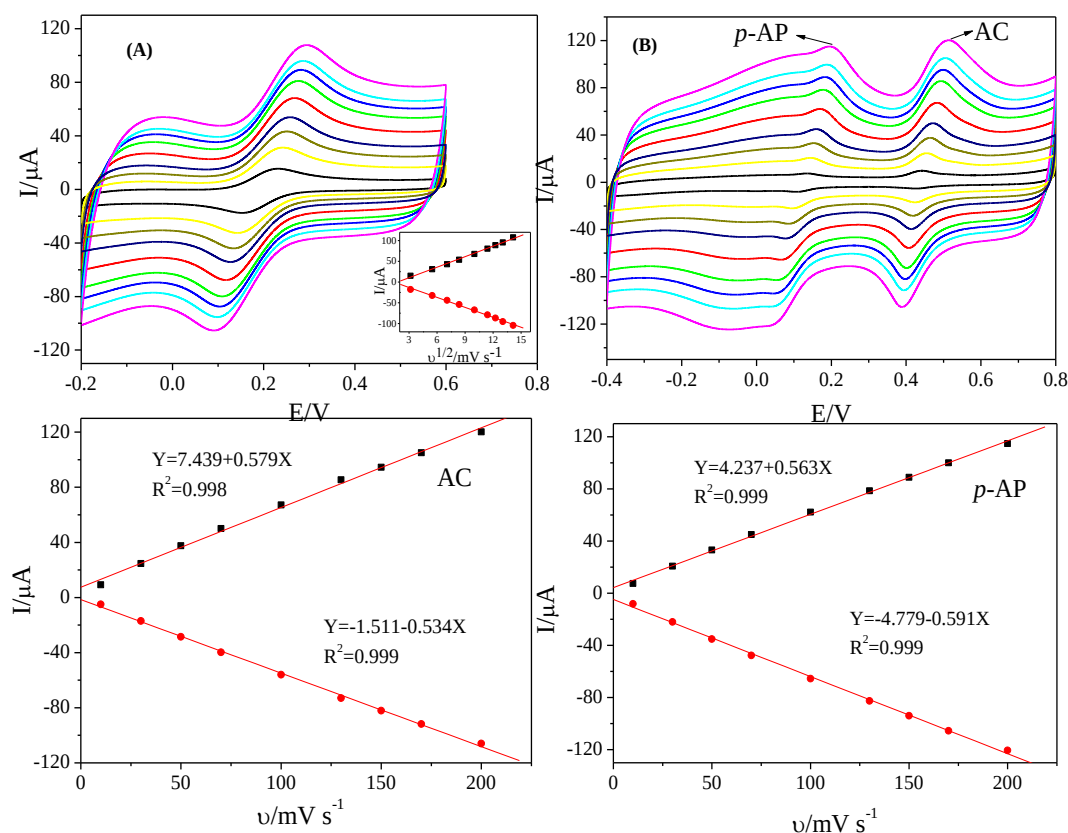


Figure 6. CV curves for β -CD-NHCO-f-GS/MWCNTs/GCE at different scan rate (10, 30, 50, 70, 100, 130, 150, 170, 200 mV s^{-1}) in an aqueous solution of 5.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ with 0.1 M KCl (A). Inset: The peak current relation with the scan rate. Cyclic voltammograms for the electrochemical response of 6 mM *p*-AP and 6 mM AC of different scan rates at the β -CD-NHCO-f-GS/MWCNTs/GCE in 0.1 M pH 6.0 PBS (B); The peak currents of *p*-AP (C) and AC (D) against the scan rates.

It is well known that the scanning rate has an effect on the redox reaction on the electrode surface. Figure 6A represents the CV curves of the β -CD-NHCO-f-GS/MWCNTs/GCE at different scan rates. The effective surface area of the modified electrode can be calculated by using the Randles-Sevcik equation [40]:

$$I_p = 2.69 \times 10^5 AD^{1/2} n^{3/2} \nu^{1/2} c$$

Where I_p is the peak currents (A), A is the effective surface area (cm^2), D ($6.67 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of $\text{K}_3[\text{Fe}(\text{CN}_6)]$, n is the number of electron transfer ($n=1$), ν is the scan rate (V/s) and c is the bulk concentration of $\text{K}_3[\text{Fe}(\text{CN}_6)]$ (mol/cm^3) [41]. The inset picture of Figure 6A shows the scanning rate is linear with the square root of the peak oxidation current. The slope of the $I_p - \nu^{1/2}$ curve is $2.771 \times 10^{-4} (\text{A.s}/\text{V})$, which is used in the above equation to calculate the effective surface area. The effective surface area is 0.0799 cm^2 , which is larger than that of bare GCE. Figure 6B displays the CV curves of 6 mM p -AP and 6 mM AC the β -CD-NHCO-f-GS/MWCNTs/GCE with a scan rate from 10 mV to 200 mV in 0.1 M PBS (pH 6.0). Figure 6 (C and D) shows a good linear relationship between the peak currents and scan rates for p -AP and AC. The peak currents of p -AP and AC increase with the increase of scanning rates. It also concludes that the electrochemical behaviors of p -AP and AC are controlled by the adsorption process.

3.4 Differential pulse voltammetry (DPV) determination of p -AP and AC

DPV is one of the most sensitive electrochemical techniques. In this study, the DPV was determined by keeping the concentration of one analyte constant and increasing the concentration of another analyte. Figure 7A shows the DPV of AC at the β -CD-NHCO-f-GS/MWCNTs/GCE in 0.1 M pH 6.0 PBS in the presence of 6 mM p -AP. It can be seen from the figure that the peak currents increase with the adding of AC, while the peak currents and peak potentials of p -AP are almost unchanged.

The linear relationship between the peak currents and different concentrations of AC are shown in Figure 7B. It is a two-stage linear relationship and the regression equations are $I_{AC} (\mu\text{A}) = 70.93 + 1.197 C (\mu\text{M})$ ($R^2=0.99$) (0.6 mM to 9 mM) and $I_{AC} (\mu\text{A}) = 87.093 + 0.114 C (\mu\text{M})$ ($R^2=0.99$) (15 mM to 0.44 mM). Similarly, Figure 7C shows the DPVs of p -AP at the modified electrode in 0.1 M pH 6.0 PBS in the presence of 1 mM AC.

The peak currents increase with the adding of p -AP, but the peak currents and potentials of AC almost remain the same. It reveals that the modified electrode can effectively detect p -AP without interference in the presence of AC. Fig. 7D displays a good linear relationship between the peak currents and the concentrations with two regression equations of $I_{p-AP} (\mu\text{A}) = 85.817 + 0.111 C (\text{mM})$ ($R^2=0.97$) (1 mM to 77 mM) and $I_{p-AP} (\mu\text{A}) = 95.556 + 0.0126 C (\text{mM})$ ($R^2=0.99$) (0.12 mM to 1.32 mM). It is also found that the slopes of linear responses of the modified electrode to p -AP and AC are greater at low concentration than at high concentration, which indicates that the sensor was more sensitive to p -AP and AC at low concentration. The reasons may be as follows: when the concentration of p -AP and AC is low, the electrode response will change significantly due to the diffusion effect on the electrode surface. At the same time, p -AP and AC can be rapidly converted to product at low substrate level, which makes the electrode display high sensitivity.

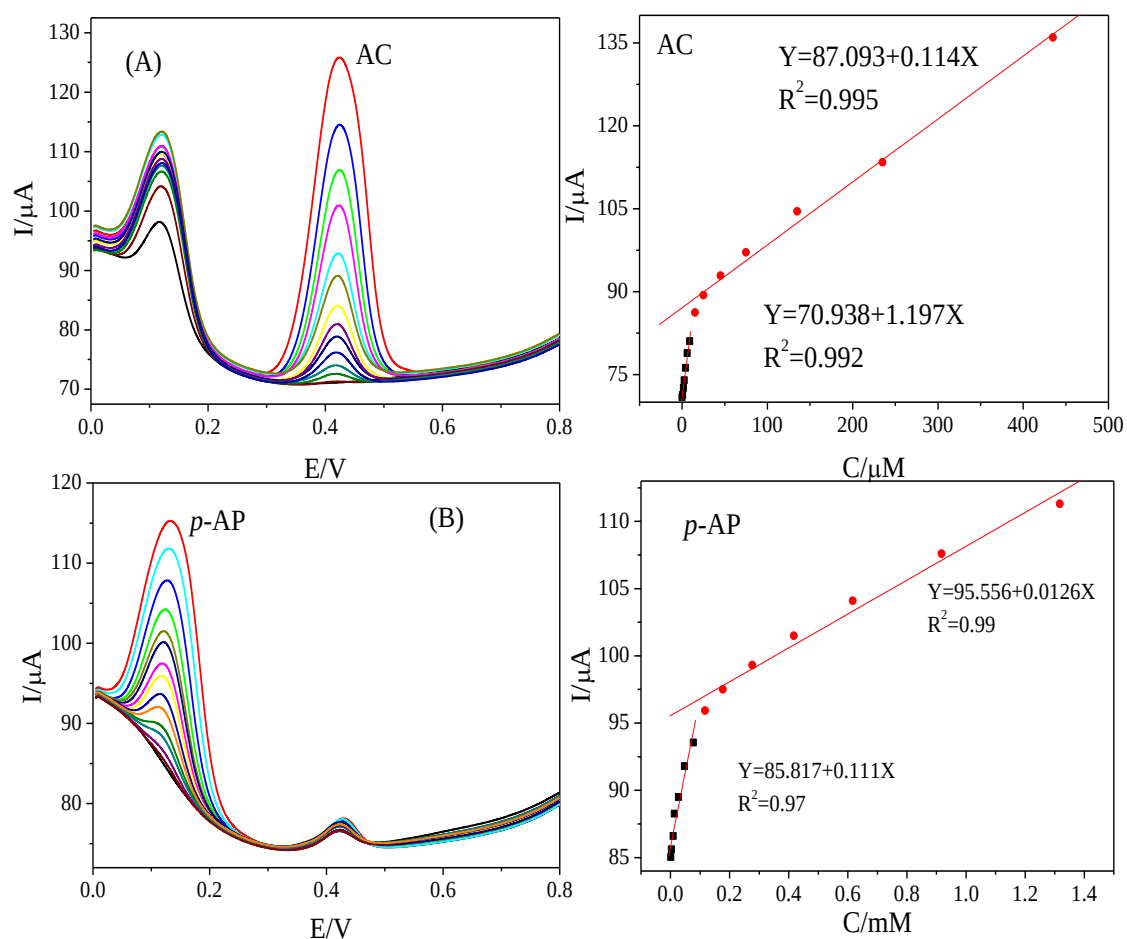


Figure 7. DPVs at the β -CD-NHCO-f-GS/MWCNTs/GCE in 0.1 M pH 6.0 PBS containing 6 mM *p*-AP and different concentrations of AC (A); containing 1 mM AC and different concentrations of *p*-AP (B).

The detection limit can be calculated according to the formula: $\text{LOD}=3S/m$ [43]. Where S is the blank standard deviation (0.004 mA for *p*-AP; 0.06 mA for AC), and m is the slope of the calibration curve (0.111 mA/ μM for *p*-AP; 1.197 mA/ μM for AC). Therefore, the detection limits of *p*-AP and AC are 0.11 μM and 0.15 μM , respectively. The electrochemical redox mechanism of *p*-AP and AC at the β -CD-NHCO-f-GS/MWCNTs/GCE is shown in Scheme. 1 [3]. Compared with other modified electrodes, this electrode has obvious advantages in detection limit and linear range (Table. 1).

Table 1. Comparison of different electrodes used in simultaneous determination of *p*-AP and AC.

Electrode	Linear range (mM)		Detection limit (mM)		Ref
	AC	<i>p</i> -AP	AC	<i>p</i> -AP	
CuO-Au/MWCNTs/GCE	0.2-6.0	0.5-1.6	0.02	0.11	[3]
Au/Pd/rGO/GCE	1.0-250	1-300	0.3	0.12	[44]
ZIF-67/MWCNT-COOH/Nafion/GCE	0.1-100	0.2-200	0.07	0.01	[45]
PEDOT/GCE	1.0-100	4.0-320	0.4	1.2	[46]
RGO-TiN/GCE	0.06-700	0.05-500	0.2	0.013	[47]
β -CD-NHCO-f-GS/MWCNTs	0.6-440	1.0-1320	0.15	0.11	This work

This can occur for the following reasons: (1) The nanohybrid β -CD-NHCO-f-GS/MWCNTs are porous on the electrode surface. Compton's team reported that this porous structure is conducive to the electrochemical identification of substances with similar oxidation potentials [40]. (2) The host guest recognition reaction of NH_2 - β -CD increases the response performance of the modified electrode. Moreover, compared with CD, NH_2 - β -CD can be protonated under acidic conditions, and can be better combined with negatively charged guest molecules. (3) The good conductive nature and large surface area of β -CD-NHCO-f-GS/MWCNTs promote the performance of the electrochemical sensor.

3.5 Interference and stability

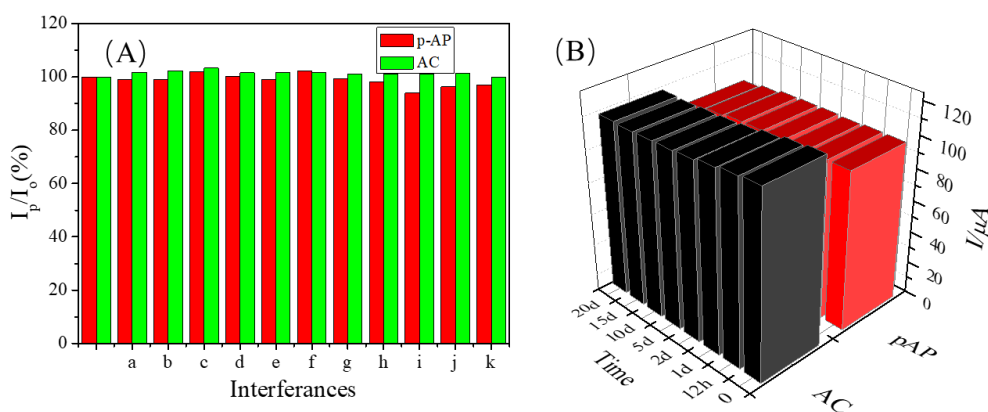


Figure 8. Corresponding currents percentage of the sensor in 0.1 M pH 6.0 PBS containing 6 mM *p*-AP and 1 mM AC and different interfering species (from a to h: Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , NO_3^- , SO_4^{2-} , H_2PO_4^- , catechol, resorcinol, *p*-nitrophenol) (50-fold inorganic coexisting substances and 5-fold organic coexisting substances) (A); Study of the stability tested with the proposed sensor (B).

Anti-interference ability is an important parameter to measure the quality of electrochemical sensors. In this work, the anti-interference ability is implemented in such a way that whether the peak currents of *p*-AP and AC will change due to the addition of catechol, resorcinol, *p*-nitrophenol and other

coexisting inorganic substances (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , NO_3^- , SO_4^{2-} , H_2PO_4^-) (50-fold). The experimental results show that the peak currents of *p*-AP and AC are not disturbed by the above compounds (Fig. 8A). The result demonstrates that the β -CD-NHCO-f-GS/MWCNTs/GCE has good selectivity and anti-interference ability. The stability of the electrochemical sensor is achieved by detecting the response of DPV to the same concentration of *p*-AP and AC every few days. The oxide peak currents are observed to be retained 96.2% and 94.4% after 20 days (Fig. 8B).

3.6 Recovery test

To check the applicability of the sensor to an actual sample, a recovery test for *p*-AP and AC in river water (from Liucang River, Bijie, China) was carried out under optimal experimental conditions by the standard addition method and DPV technology. The experimental results are shown in Table. 2, which indicates that the recovery is acceptable and desirable.

Table 2. The simultaneous determination of *p*-AP and AC in real samples.

Samples	Added (mM)	Found (mM)	Recovery (%)
AC	40.0	44.5	111.3%
	60.0	57.8	96.3%
<i>p</i> -AP	40.0	41.2	103.0%
	60.0	58.5	97.5%

4. CONCLUSIONS

In this work, a β -CD-NHCO-f-GS/MWCNT nanocomposite was successfully prepared and used to establish a sensitive electrochemical sensor for the simultaneous determination of *p*-AP and AC. FTIR, SEM, XPS, CV and DPV were used to analyze the results of physicochemical and electrochemical characterization. These results demonstrate that the β -CD-NHCO-f-GS/MWCNT composite has a large surface area, high conductivity and good electrocatalytic performance for *p*-AP and AC. The simple process, fast measurement speed, high precision, wide linear range, low detection limit, high stability and high recovery rate for this sensor prove that it has great application prospects.

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