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Sensitive and Selective Determination of Chloramphenicol on Ordered Mesoporous Carbon/Nafion Composite Film

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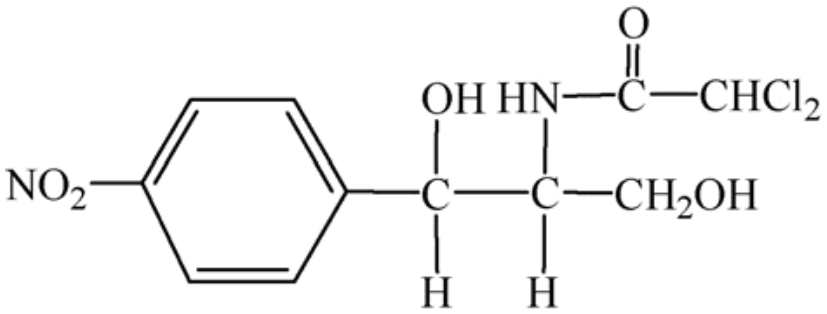
We report a method of selectivity and sensitivity measurement of chloramphenicol on glassy carbon electrode modified by ordered mesoporous carbon (OMC)/Nafion composite film. In an ethanol solution containing 0.5% Nafion, the insoluble OMC was well dispersed, thereby producing a stable, good dispersion of the OMC/Nafion suspension. After ethanol was evaporated, a homogeneous OMC/Nafion composite film-covered GCE was obtained. Cyclic voltammetry (CV) studies reveal that OMC remarkably enhances the electrocatalytic activity toward the reduction of CAP when 0.001% sodium dodecyl sulfate (SDS) is present, which led to considerable improvement of cathodic peak current for CAP at −0.75 V (versus 1.0 M KCl-Ag/AgCl) in 0.01 M pH 7.4 phosphate buffer solution (PBS) containing 3 mM $NaNO_3$. At the optimum conditions, the calibration curve was linear in the concentration range 5.0×10^{-7} – 6.0×10^{-5} mol L^{-1} with the detection limit of 8.5×10^{-9} mol L^{-1} (S/N=3) by linear scan stripping voltammetry (LSSV). The electrode was successfully used to detect CAP directly in honey samples. In addition, the electrochemical reaction mechanism and kinetic parameters for reduction of CAP on OMC/Nafion film were studied.

Keywords: Mesoporous carbon, Electrocatalysis, Chloramphenicol, Electrochemical sensing

1. INTRODUCTION

Chloramphenicol (CAP), a broad spectrum antibiotic, which has a strong antibacterial effect against Gram-positive and Gram-negative bacteria [1]. Its chemical structure is as shown in Scheme 1.



Scheme 1. Chemical structure of CAP.

The drug was separated from Streptomyces venezuelae in 1947 and it has been widely used to treat serious infections such as typhoid fever and other forms of salmonellosis. Because of its toxic side effects, CAP has been found to cause serious health problems in humans, so that clinical application for CAP is controlled and its residues in food producing animals have been strictly prohibited in many countries including in the European Union (EU) and United States (US) [2.3], and a limit value of 1 ppb was set in condition of foods imported from other countries by EU, Switzerland, and US. So sensitive, qualitative and quantitative methods of detecting CAP are required for monitoring the level of it. Currently, the determination methods of CAP in different biological samples have been reported. Such as HPLC or HPLC with MS [4-6], CAP immunosensor based on nanoparticles [7-8], CAP aptasensor with colorimetric detection and fluorescence [9-10], capillary electrophoresis with diode array detection [11].. Despite the high sensitivity and accuracy of these methods, their expensive equipments, complex pre-treatment of samples and time consuming limit their widespread application. Electrochemical methods are simple, rapid, sensitive and low-cost[12-13], which are suitable for measurement of trace CAP. Other groups developed some electrochemical sensors based on the nanotube for the detection of CAP [14-15]. Yang *et al.* prepared a carbon paste electrode containing MoS_2 - polyaniline for determination of CAP with differential pulse voltammetry, the linear range was 0.1 to 1000μM and the detection limit was 6.5×10^{-8} M [16]. But the practical application of these electrochemical methods can't satisfy the direct determination of CAP in the biological samples. As far as we know, the direct detection of CAP in the honey sample on glassy carbon electrode modified by ordered mesoporous carbon (OMC) / Nafion composite film has not been reported.

OMC, a new type of carbon material, has many excellent properties such as high surface areas[17], large pore volume[18], large adsorption capacity[19], size selectivity and widely open ordered structure[20–21]. These attractive properties have been exploited in designing novel electrochemical sensors and biosensors. Zhou group reported the electrochemical behaviors of eight kinds of electroactive compounds at OMCs/GCE, which has more favorable electron transfer kinetics than that at CNTs/GCE [22]. Zhu *et al*. reported the electrochemical behavior of NADH at a Nile blue/OMC electrode. A new well defined redox couple appeared, showing that OMC significantly catalyzes the oxidation of NADH [23]. Our group has developed an OMC/Nafion film electrode and a

self-assembled alkanethiol electrode based OMC adsorbed [24-25], which can satisfy the detection of real biological samples.

Here we report a kind of selective and sensitive determination of CAP at glassy carbon electrode modified by OMC/Nafion composite film. Compared with the previous reports, the proposed determination method of CAP has an advantage of prepareing the OMC/Nafion film electrode. Furthermore, the ability of anti-interference for the electrode is so powerful that the CAP in the honey samples can be directly determined without any pretreatment. Additionally, both the adsorption behaviors and the reduction mechanism at the OMC/Nafion composite film electrode in different pH values have been studied.

2. EXPERIMENTAL SECTION

2.1. Regents and materials

CAP was purchased from Guangzhou qiyun biology technology Co., Ltd (Guangzhou, China) and SDS from Biolife Science & Technology Co., Ltd (Shanghai, China). Other chemicals were of analytical reagent grade and used directly without purification. All solutions were prepared with ultrapure water.

2.2. Apparatus

Electrochemical experiments were performed on a LK6200 Electrochemical Workstation (BioNano International Singapore Pte., Ltd.) with a bare or modified GCE working electrode, a platinum counter electrode and an Ag/AgCl (1.0 M KCl) reference electrode. Before the electrochemical experiments, purge with nitrogen into the solution for 20 min to remove dissolved oxygen. All experiments were performed at room temperature (ca. 25 °C). The structure and morphology of OMC was observed by scan electron microscope (SEM) with a NoVa^{TM} Nano SEM 430 (FEI Company, Netherlands).

2.3. Synthesis of the OMC and electrode preparation

The synthesis of OMC was according to previous reports[26]. With the aid of ultrasonication for 30 minutes, 1 mg of the as synthesized OMC was dispersed into the 1mL ethanol to give a uniform black suspension. Before the modification of surface, the 3 mm GCE should be pretreated by being polished with 3 μm alumina slurries, being cleaned in ethanol and ultrapure water, successively. The OMC/Nafion composite film was prepared by throwing a 5 μL 0.5 wt% Nafion solution and 5 μL 1 mg mL^{-1} OMC suspension successively onto the GCE. At last, evaporating the solvent at room temperature in air. Electrode thus prepared was called OMC/Nafion/GCE.

2.4. Analytical procedure

The new OMC/Nafion/GCE needs to be activated before use. Activation peformed in PBS buffer solution (0.01mol L^{-1}, pH 7.4) containing $NaNO_3$ (3 mM) and SDS (0.001%) by CVs.until stable response was obtained. And then transferred into another 10 mL of PBS-$NaNO_3$- SDS solution containing a certain concentration of CAP. After an accumulation for 240 s at 0 V, the LSSV from -0.6 V to -1.2 V at a scan rate of 100 mV s^{-1} was recorded for the determination of CAP. After each measurement, the modified electrode need to be scanned by CV for three times successively in a black solution to make the electrode regenerated. The honey samples were determined directly in the same procedure without any pretreatment. All experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of OMC

Typical SEM image of the OMC recorded is shown in Fig. 1.

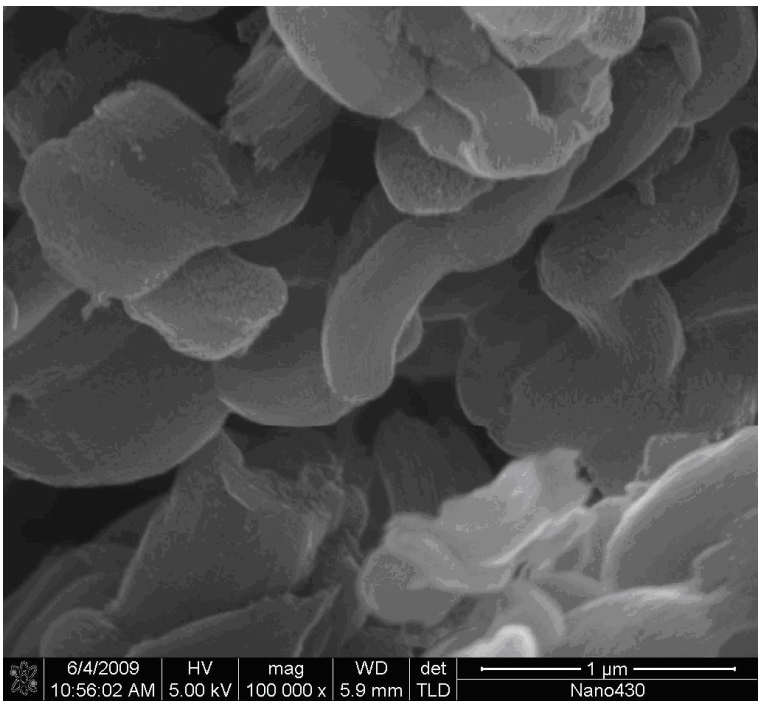


Figure 1. SEM image of OMC

Based on SEM observation, flake like particles with 0.1-1 μm was observed. Though the pristine mesoporous structure can not be discerned due to the lower resolution of SEM, the

congregation of OMC has a typical three-dimensional porous microstructure, so it possesses a larger plane edges, which are more suitable for the electrochemical reaction.

3.2. The voltammetric behavior of CAP at the OMC/Nafion/GCE

First , 5 mM $K_3[Fe(CN)_6]$ containing 0.5 M KCl was used as electrochemical probe to evaluate the electrochemical characteristics of the OMC/Nafion composite film. For OMC/Nafion/GCE, CV of different scan rates is shown in Fig.2.

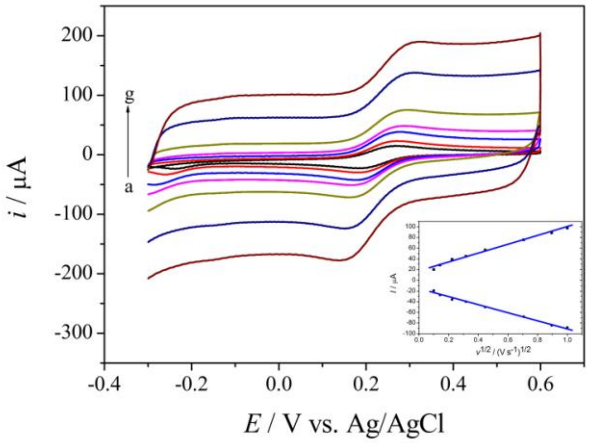


Figure 2. CVs of 5 mM $K_3[Fe(CN)_6]$ on the OMC-Nafion/GCE at different scan rates about 10，20，50, 100, 200, 500, 800 and 1000 mV s^{-1} (from a to g) in the 0.5 M KCl solution. Inset: plots of redox peaks current (i_p) vs. scan rate (v).

The difference between E_{pa} and E_{pc} ($\triangle E_p$) is estimated to be 85 mV at the scan rate of 50 mV s^{-1}, which indicated that the electron transfer kinetics for OMC/Nafion/GCE is a quasireversible redox process. The redox peaks currents are in direct proportion to the square root of scan rate in the range from 0.01 to 1 V s^{-1}, i_{pa} (μA)= -74.157 $v^{1/2}$(Vs^{-1})-16.137 (r = 0.9960)， i_{pc} (μA)= 81.126 $v^{1/2}$(Vs^{-1})+117.661 (r = 0.9950), indicating that the currents are controlled by a semi-infinite linear diffusion process. For the OMC/Nafion/GCE, the electrochemical active areas were estimated through 5 mM ferricyanide as the probe. According to the Randles–Sevcik equation: $i_p = 2.69\times10^5\ n^{3/2}v^{1/2}D^{1/2}AC^0$, where C^0 = 5 mM and $D = 0.76\times10^{-5}$ cm^2 s^{-1} [27] is the concentration and diffusion coefficient of ferricyanide, respectively, and others parameters have their conventional senses. The electrochemical active area for OMC/Nafion/GCE was calculated to be 0.0675 cm^2. The roughness factor was 2.15 for the OMC/Nafion/GCE and 1.87 for GCE. The result indicates the electrochemical area on OMC/Nafion was larger than that on GCE.

Cyclic voltammogram of CAP at the (A) bare GCE or (B) OMC/Nafion/GCE in PBS with pH 7.4 at the scan rate of 100 mV s^{-1} are shown in Fig. 3 (blue solid line). CAP has a peak currents either on bare GCE (Fig. 2A, blue solid line) or on OMC/Nafion/GCE (Fig. 2B, blue solid line).

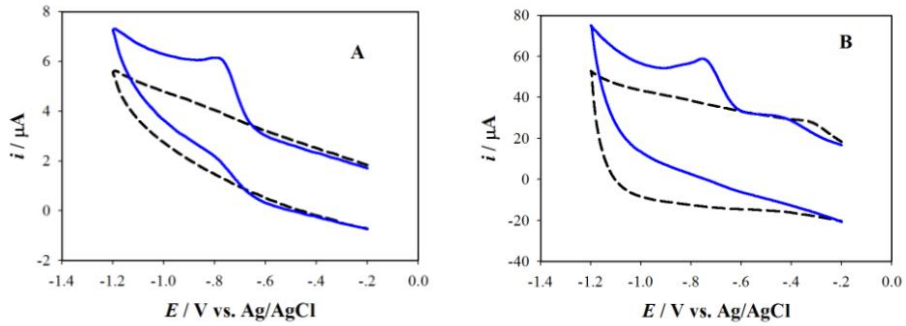


Figure 3. CVs of (A) bare GC or (B) OMC/Nafion/GCE in PBS (pH=7.4) solutions without (dotted line) or with 0.05 mM CAP (blue solid line). Scan rate: 100 mV s^{-1}.

However, cathodic peak current for CAP on OMC/ Nafion / GCE was at −0.75 V and on GCE was at -0.78V. In comparison with GCE, peak potential shifted negatively for about 27mV and peak current at OMC/Nafion/GCE is significantly increased for about 10 times larger than that at GCE (notice the different scale bar). It indicated that OMC had stronger electrocatalytic effect to the reduction of CAP.

Voltammetric responses of 0.5 mM CAP cycle twice on the OMC/Nafion /GCE in pH 7.4 PBS solution are shown in Fig.4.

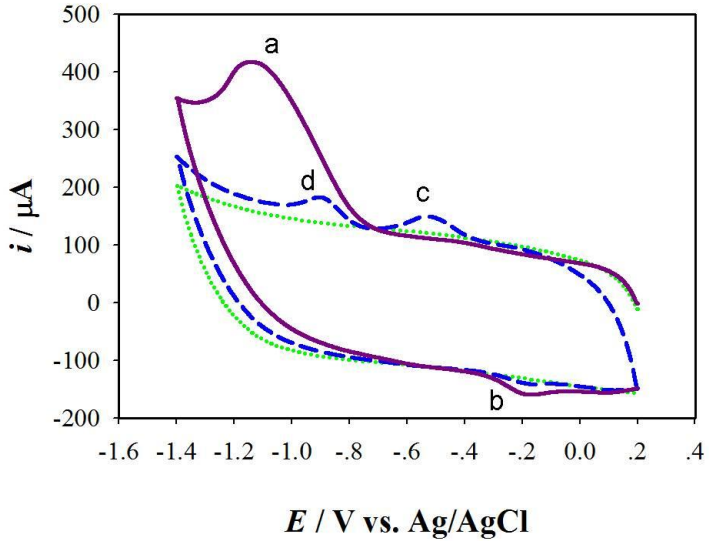


Figure 4. CVs of OMC/Nafion/GCE in PBS (pH=7.4) solutions containing 0.0 (dotted line) and 0.5 mM CAP (long dash line and solid line). Scan rate: 100mV s^{-1}, first cycle (solid line), second cycle (long dash line)

As we all can see from Fig.4, when the potential is first scaned in negative direction, a large and well-shaped cathodic peak (a) appears at about −1.1V. While backword scans, an anodic peak (b) occurs at -0.17 V. When cycle scans again, producing a new cathodic peak (c) with the potential of −0.52 V, and the original cathodic peak (a) fell largely to the peak (d) and the peak potential shifts

negatively to -0.89 V, indicating a strong adsorption effect on the electrode. According to the currently accepted mechanism, peak (a) is the result that nitro group (NO_2) is irreversible reduced to a hydroxylamine group (NHOH), while peaks (b) and (c) are due to the redox of NHOH group to nitroso group (NO) [28-29]. Since the cathodic peak (a) is more sensitive, we chose it to detect CAP .

3.3. The effect of pH and the supporting electrolyte on the reduction of CAP

The effect of the solution pH on the peak currents and peak potentials of CAP reduction was investigated in the range of pH 1.0-13.0 using a 0.1M HCl, 0.01 M Britton-Robinson (B-R) buffer solution and 0.1 M NaOH.

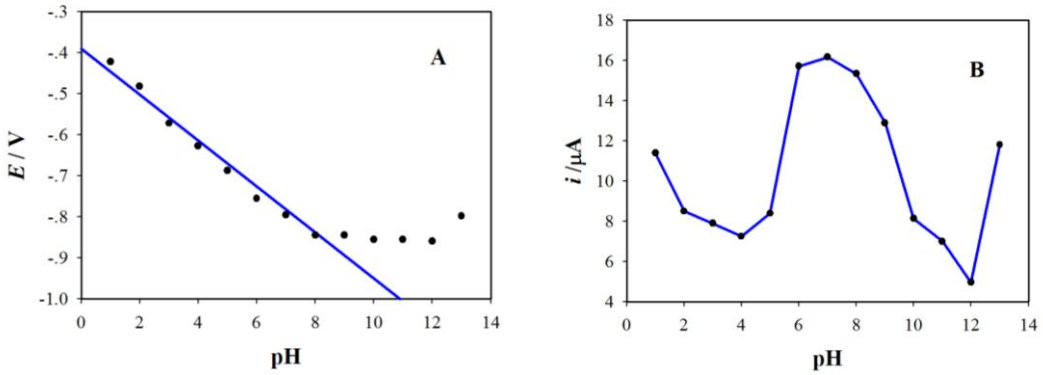


Figure 5. Variation of (A) the cathodal peak potential (E_{pc}) and (B) cathodal peak current (i_{pc}) with the solution pH for 0.05 mM CAP.

Fig. 5A shows the dependence of the cathodic peak potential (E_{pc}) for CAP (0.1 m M) with pH. The peak potential (E_{pc}) of CAP presents almost a linear change in the negative direction, when pH varied between 2.0–8.0, which means that the proton plays a decisive role in the reduction process of the CAP.. Linear relationship between E_{pc} (in V) and the pH was : E_{pc} = -0.3821-0.0598 pH, and the linear correlation coefficient is 0.9960. The peak potential slope of 0.0598 V pH^{-1} shows that the electron transfer is accompanied by an equal number of protons. When pH was increased in the range of 8.0–12.0, the peak potentials (E_{pc}) for CAP kept unchanged, indicating that the rate determination step of the reduction reaction of the CAP is independent of the protons. However, the peak potentials (E_{pc}) for CAP decreased to -0.8V in 0.1 M NaOH. This may be the cause of single electron transfer process of the CAP reduction reaction in the absence of proton, which is consistent with the reported literature [30]. the electrochemical equation may be as follows:

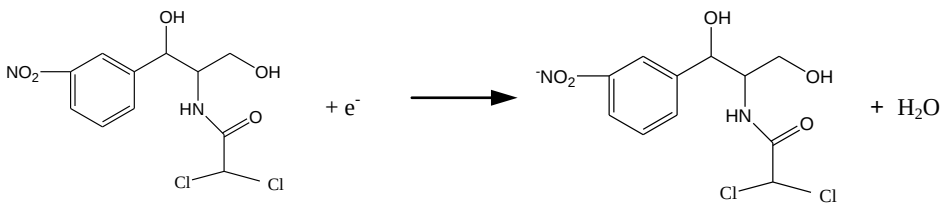


Fig.5B shows the influence of the pH on the peak current. The peak current of CAP decreases when pH is raised in the range of pH 1.0–4.0. When pH varies between pH 4.0 and 6.0, and greater than pH 12.0, the current rises dramatically. When pH rises in the range of pH 8.0-12.0, the peak current of CAP decreases. However, the peak current increases slightly and reached the maximum in the pH range of 6.0–8.0, indicating that CAP is suitable for the sensitive determination in neutral solution.

Some buffer solutions including PBS (pH 7.4), B-R and NH_3–NH_4Cl (each 0.01M) were also discussed. The results showed that peak currents of CAP in PBS buffer solution is higher than any other solutions. Some supporting electrolytes such as $NaNO_3$, KNO_3, NaCl and KCl were also studied. When the PBS buffer solutions contained 3 mM $NaNO_3$, the peak current of CAP was stable and well-shaped. So the solution of 0.01M PBS (pH 7.4) including 3 mM $NaNO_3$ was used in the following studies.

3.4. The influence of surfactant

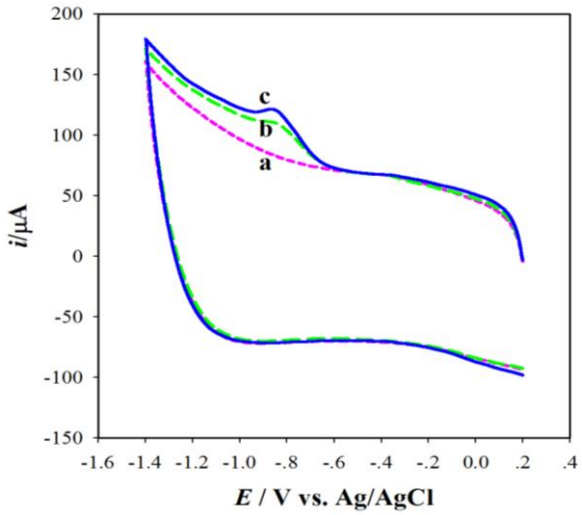


Figure 6. CVs of OMC/Nafion/GCE in PBS (pH=7.4)-$NaNO_3$-SDS solutions containing 0.0 (a, purple dotted line) and 0.05 mM CAP without SDS (b, green long dash line) and 0.5 mM CAP (blue solid line). Scan rate: 100 mV s^{-1}.

Surfactants are widely used in electrochemical analysis to improve the electrode/solution interface, so that it has stronger ability of dissolution and sensitivity [31, 32]. Some surfactants such as octylphenylpolyethylene glycol (OP), dodecyl trimethyl ammonium bromide (DTAB), cetyl trimethyl ammonium bromide (CTAB), Tween-80 and SDS were investigated by CV in our studies. All surfactants can enhance the peak currents. However, the role of SDS is much stronger (Fig. 6), and then it is CTAB, Tween-80, DTAB, OP, successively. The results reflect the role of sodium ion, cetyl trimethyl group and dodecyl trimethyl group in the reduction of CAP in the presence of OMC. When 0.001% SDS was in the solution, peak currents increased by almost 40% than the solution in which had no SDS (Fig.5). So 0.001% SDS solutions were used in our studies.

3.5. Effect of scan rate on the peak currents and peak potential

Electrochemical mechanism and other relevant information can be obtained from the relationship between peak current and scan rate. Therefore, the electrochemical behaviors of CAP at different scan rates have been studied on the surface of the OMC/Nafion/GCE (Fig. 7). The linear equation between the peak current i_p (in μA) and the square root of the scan rate $v^{1/2}$ (in mV s^{-1}) in the range of 10–100 mV s^{-1} was found to be: i_p=2.5051$v^{1/2}$ - 4.1777, with a correlation coefficient of 0.9990, which indicated that the reduction of CAP corresponds to a diffusion-controlled process [33]. However, it seems to be inconsistent with the fact of CAP enrichment on the electrode. It may be associated with the diffusion of CAP in the surface of OMC/Nafion film. The peak potential shifted negatively as the scan rate increased. The dependence of reduction peak potential as function of scan rate can be illustrated by the following equation: E_{pc}= - 0.1453 lg v - 0.5743 (r = 0.9948, E_{pc}: V, v : mV s^{-1}).

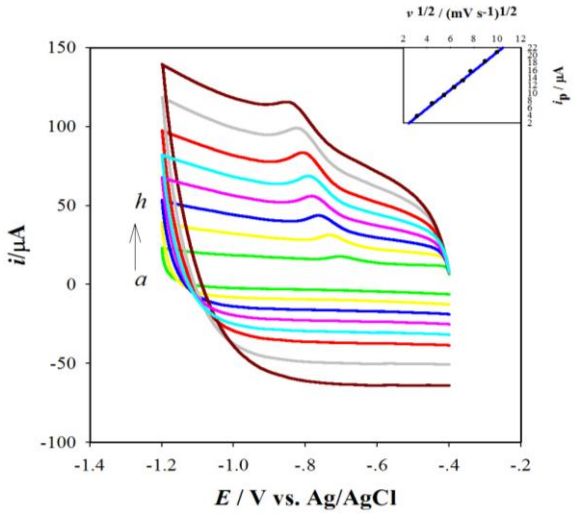
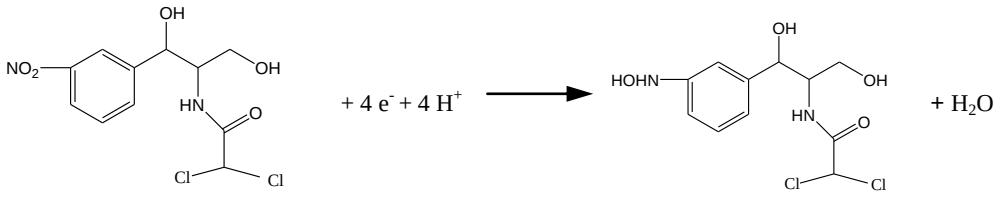


Figure 7. CVs of 0.05 mM CAP on the OMC/Nafion/GCE in PBS-SDS-$NaNO_3$ solution (pH 7.4). From *a* to *h*, scan rate of 10, 20, 30, 40, 50, 60, 80, and 100 mV s^{-1} respectively. Insets: plots of i_{pc} versus $v^{1/2}$ in the present of 0.05 mM CAP.

According to Laviron's theory [34], the slope was equal to 2.303RT/ $an_\alpha F$, so the αn_α in the experiment is equal to 0.4070. For a total irreversible electrode reaction process, it may be assumed that the electron transfer coefficient (α) is roughly 0.1, so the value of n_α is calculated to be 4, suggesting that reduction reaction of CAP is related to four electrons transfer process. This is in accordance with previous reported in literature [28]. While the electron transfer rate constant (k_s) is calculated to be 10.6 s^{-1}. Since CAP reduction is accompanied by the transfer process of the equal amounts of electrons and protons, therefore, the reaction occurring at the electrode is four electrons and four protons transfer reaction. The electrochemical equation is as following:



3.6. Effect of accumulation potential and accumulation time

Accumulation potential and accumulation time are two important paramaters in linear sweep stripping voltammetry (LSSV) technique. Whether appropriateness or not of the two paramaters will affect the amount of adsorption and the measurement sensitivity of CAP at the electrode. Prolong the accumulation time, the peak current of peak (a) increases and the peak potential shifts negatively. In a solution containing 0.1 mM CAP, when the accumulation time is more than 240 s, the peak currents reach a maximum value and remain a platform. The results show that the adsorption or extraction of CAP on the OMC/Nafion/GCE achieved an equilibrium process. So the accumulation time selected is 240 s in our study. When the accumulation potential was tested in the range of -0.40 - 0 V, the peak current of peak (a) increased. However, when the accumulation potential was changed from 0V to 0.9 V continuously, the peak current of peak (a) remained almost constant, suggesting that the adsorption of CAP was up to saturation and no significant adsorption produces within the potential scope. So the accumulation potential is performed at 0 V.

3.7. Calibration curve

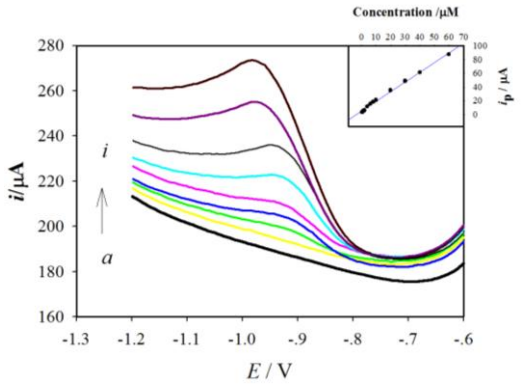


Figure 8. LSSV of CAP with different concentration of CAP. From *a* to *i* the concentration correspond to CAP of 0, 0.9, 2, 8, 10, 20, 30, 40 and 60 μM.

LSSV was used for the determination of CAP on the OMC/Nafion/GCE and the results are shown in Fig.8., As can be seen from Fig.8, linear relationship between values of the peak current and concentration of CAP is obtained in the range of 0.5-60 μM, and the linear equation is: i_p (μA) = 1.4156 c + 4.6811 (μM), r = 0.9973. When CAP was accumulated at 0 V for 240 s, the detection limit is calculated as 8.5×10^{-9} M (S/N=3). After each measurement, the modified electrode cycles from −0.6 to −1.2 V for three times to get regeneration in a blank solution.

3.8. Repeatability, reproducibility and selectivity

To estimate the repeatability and reproducibility of OMC /Nafion/GCE, a solution containing 5μM CAP was detected for 10 times by the same modified electrode, and the relative standard derivation (R.S.D.) for the peak current was 2.9%. In Addition, a solution containing 5μM CAP was measured by 5 modified electrodes prepared with the same method and the R.S.D. for the peak current was 2.0%. When the same modified electrode was used to detected the solution containing1.0×10^{-4} M CAP by cyclic voltammetry for one month, the peak current only declined by 3.1%. It indicated that the electrode is very stable and has long lifespan and well repeatability.

The interference of some coexistent material to the CAP assay is also studied. The results show that in the solution containing 0.02 m M CAP, at least 50-fold of ascorbic acid, K^+, Ca^{2+}, Cl^-, Fe^{3+}, 10-fold of Cu^{2+}, ofloxacin, norfloxacin, ciprofloxacin, sulfamethoxaxol, trimethoprim, melamine do not interfere with the measurement of CAP.

3.9. Determination of chloramphenicol in honey samples

Finally, The new method is applied to the detection of chloramphenicol in honey samples. According to the report [35], CAP should be extracted with ethyl acetate from honey samples followed by analysis. However, CAP in honey can be directly determined without any pretreatment in our studies. Honey samples were prepared as follows: the samples were purchased in a local supermarket, an amount of 2 ml of honey samples were diluted by pH 7.4 PBS-$NaNO_3$-SDS solution, various amounts of CAP stock solution were sparked into it to obtain different biological samples. The results are shown in Table 1. The satisfactory recoveries of the experiment for CAP by standard addition method are between 96.50% and 103.6%.

Table 1. Determination results of CAP in honey sample

Sample	Number	Added(μM)	Found (μM)	Recovery (%)
A	1	4.00	4.02	100.5
	2	8.00	8.03	100.4
B	1	4.00	4.08	102.0
	2	8.00	8.29	103.6
	3	20.00	19.5	97.50
C	1	4.00	3.92	98.00
	2	8.00	7.79	97.38
D	1	4.00	4.13	103.3
	2	8.00	7.72	96.50

4. CONCLUSIONS

Here we use the OMC to prepare a new OMC-Nafion film modified glassy carbon electrode. The resulting electrode facilitated measurement of CAP with good stability and accumulation function.

The strong electrocatalytic ability of OMC greatly enhances the reduction current of CAP, which was probably owning to the larger effective surface area and the stronger adsorption ability of OMC/Nafion/GCE. CAP in the real biology sample was determined and satisfactory results were obtained using the modified electrode. Thus, OMC/Nafion composite film has high sensitivity and it is expected to be used as electrochemical sensors.

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