

# Silver Nanoparticles/Carboxylic Short-Chain Multi-Wall Carbon Nanotubes as Electrochemical Sensor for Ultrasensitive Detection of Chloramphenicol in Food

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Received: 8 May 2019 / Accepted: 4 July 2019 / Published: 5 August 2019

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This research developed a novel electrochemical sensor for determination of chloramphenicol (CAP) in aqueous solutions. The working electrode was fabricated by carboxylic short-chain multi-wall carbon nanotubes (Short-MWNTs-COOH) and silver (Ag) nanoparticle based on glass carbon electrode (GCE). Scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS) confirmed that Ag nanoparticle had been successfully electrodeposited onto the modified electrode. Then, some experimental parameters such as pH, scan rate, deposition potential and time were optimized by cyclic voltammetry (CV) and linear sweep stripping voltammetry (LSSV). Under the optimized conditions satisfactory results attained for detection of CAP in the concentration range of 0.3-229  $\mu\text{M}$  and with the detection limit (LOD, S/N=3) of 0.049  $\mu\text{M}$ . This new electrochemical sensor showed many advantages like easy operation, low cost, and high sensitivity, which enables successful determination of CAP in real samples.

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**Keywords:** Chloramphenicol; Silver Nanoparticle; Carboxylic Short-Chain Multi-Wall Carbon Nanotubes; Electrochemical Sensor.

## 1. INTRODUCTION

Antibiotics are extensively used from 1900s in clinical medical and veterinary medicine because of their excellent bacteriostatic actions. CAP is a kind of broad-spectrum antibiotic which has been synthesized in 1947 by David Gottlieb. It can be used to treat dysentery, anthrax bacteria, mild and eye infections and has been known as a useful veterinary drug [1, 2]. However, due to its low cost and high

efficiency, CAP has been abused illegally and accumulation of this compound in food and water might lead to severe impacts on health such as aplastic anemia, cardiovascular collapse, etc. [3-5]. Nowadays, many countries have strictly controlled dosage of CAP in food and other by-products.

Therefore, it is meaningful to introduce new effective, fast and cheap methods to determine CAP. Wang, Chen, and other research groups have simultaneously detected CAP and other drugs in bovine milk by ultra-high performance liquid chromatography–tandem mass spectrometry (UHPLC-MS/MS) [6, 7]. Gas chromatography–mass spectrometry (GC-MS), liquid chromatography–mass spectrometry (LC-MS), ultrahigh performance supercritical fluid based chromatography tandem mass spectrometry, capillary zone electrophoresis, and other techniques are also introduced as effective methods for determination of this drug [8, 9]. In addition to chromatography, chemiluminescence, enzyme-linked immunosorbent assay (ELISA), molecularly imprinted polymer (MIP) and electrochemical methods have also been utilized [10-12]. However, the formers need expensive equipment and complex pretreatment. To the contrary, electrochemical methods have superior advantages such as low cost, fast response, good sensitivity, and high selectivity. Therefore, electrochemical methods are applied as the preferred methods for determination of CAP in real samples.

Carbon nanotubes is a kind of one-dimensional nanomaterial, which has many merits like good mechanical, electrical and chemical properties. In recent years, it has been applied in industrial, chemical and physical materials. Carboxylic short-chain multi-wall carbon nanotubes (Short-MWNTs-COOH) is the acidized form of carbon nanotubes, in which the incorporated carboxyl and hydroxyl groups would be beneficial for the reaction of carbon nanotubes with  $\text{NH}_3$ ,  $\text{NO}^{2-}$ , etc. Moreover, Short-MWNTs-COOH could also promote the electron transfer between materials and GCE. It has been widely used to detect lead, cupric, and cadmium ions along with dopamine, norfloxacin, etc. Ag nanodendrites contain branched dendritic structures with high specific surface area, favorable conductivity and biocompatibility [13, 14], which are extensively applied as electrochemical sensors.

In this report, Short-MWNTs-COOH is immobilized onto glassy carbon electrode (GCE) and Ag nanodendrites were electrodeposited onto the modified electrodes. SEM, EIS and CV techniques were employed to prove that Ag nanodendrites/Short-MWNTs-COOH/GCE had been prepared successfully. This methodology was constructed to develop a new route for determination of CAP in aqueous solutions.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

Chloramphenicol (> 99.0%), p-nitrophenol (> 99.0%), metronidazole (> 99.0%), thiamphenicol (> 99.0%), norfloxacin (> 99.0%), tetracycline (> 99.0%), sulfadiazine sodium (> 99.0%) and tylosin (> 99.0%) were all obtained from Aladdin Industrial Corporation in Shanghai. Short-MWNTs-COOH was acquired from Nanjing xianfeng nanomaterial technology co. LTD. KCl,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , ascorbic acid, D-glucose,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{KNO}_3$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $\text{AgNO}_3$  were purchased from Sinopharm Chemical Reagent Co., Ltd in Nanjing. Honey and Devondale milk powder

were obtained from local supermarket. Santen-FX eye drops were purchased in Japan. All solutions were prepared with double-distilled water.

## 2.2 Fabrication of the modified electrodes

Before modification of the selected materials, glassy carbon electrodes (GCE) were polished by  $\text{Al}_2\text{O}_3$  slurry, rinsed by absolute ethanol and double-distilled water for three times. Then, the prepared electrodes were dried at room temperature. Thereafter, GCE was decorated by an 8  $\mu\text{L}$  solution containing 2 mg/mL of Short-MWNTs-COOH after ultra-sonication and dried in air. Afterwards, Short-MWNTs-COOH/GCE was electrodeposited in an electrolyte solution of  $\text{AgNO}_3$  (7 mM),  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (50 mM), and  $\text{KNO}_3$  (0.1 M). The electrodeposition was developed at the potential of -0.7 V for 10 s. The modified electrode was then taken out and rinsed with double-distilled water immediately. Ag nanodendrites/Short-MWNTs-COOH/GCE was prepared when the electrode was dried. Short-MWNTs-COOH/GCE and Ag nanodendrites/GCE were modified according to the similar procedures.

## 2.3 Preparation of real samples

Before used, real samples were treated simply according to the literature [15]. A honey sample (1.0 g) was added into 10 mL solution of phosphate buffer (PB) in a centrifuge tube. Then, the mixture was mixed evenly followed by centrifuge at 12000 rpm for 10 min and pH of the supernatant was adjusted to 7. After that, the solution was transferred to a 50 mL volumetric flask and diluted with PB (pH=7.0) to the marked line. Then, 1.0 g Devondale milk powder was dissolved in 10 mL PB and fully stirred. The mixture was collected by centrifuge at 12000 rpm for 10 min and filtrated for three times, respectively. Then, pH of the mixture was adjusted to 7 and the suspension was diluted with PB to 50 mL. Finally, 5 mL Santen-FX eye drops was injected into 50 mL volumetric flask and diluted with PB (pH=7.0) to the marked line. The samples were stored at 4°C for future use.

## 2.4 Methods

Electrochemical measurements were performed on an electrochemical station (Shanghai Chenhua; Model: CHI1230C) with a three-electrode configuration including a modified electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt wire as counter electrode. EIS and CV analyses were utilized to exhibit the properties of different electrodes in KCl and  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (1:1) solution. CAP was detected by LSSV in PB with the deposition potential of -0.2 V and the deposition time of 420 s.

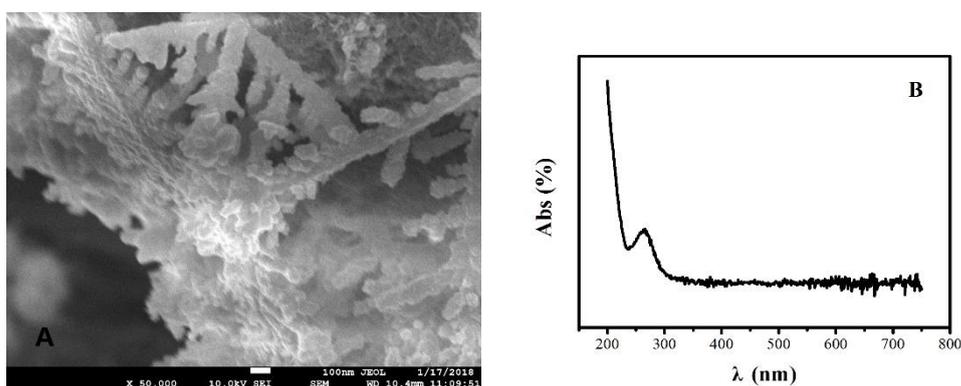
The spectrograms of Ag nanodendrites were displayed by UV-Vis (Thermo Evolution 201, American). Scanning Electron Microscope (S-3400N, Hitech Corp, Japan) was used to characterize structure of the synthesized materials. A pH meter (Mettler Toledo, Shanghai) was handled to adjust pH of PB with 0.2 M solutions of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ . HPLC (Thermo U3000, American) was applied to detect CAP in the real samples using a commercial  $\text{C}_{18}$  column (4.6 mm  $\times$  150 mm, 5  $\mu\text{m}$ , Thermo Fisher Scientific, Inc., China) operating at 25 °C and invariable elution with methanol-

water (1:1) at a flow rate of  $1.0 \text{ mL}\cdot\text{min}^{-1}$ . UV absorbance detection was performed at the wavelength of 280 nm.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of the modified electrodes

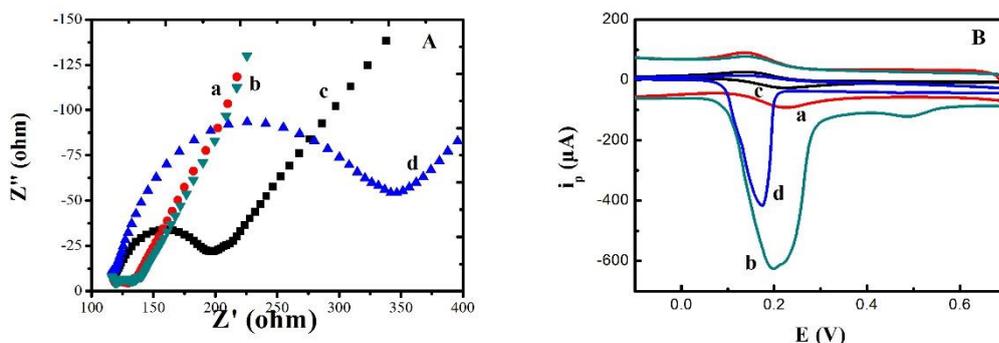
SEM was utilized to study the surface morphologies of Ag nanodendrites/Short-MWNTs-COOH/GCE (Fig. 1A). This figure displays a three-dimensional dendritic-like structure for Ag nanodendrites, which accords well with the previous publication [13]. This finding indicated that Ag nanodendrites had been synthesized successfully on Short-MWNTs-COOH/GCE. UV-Vis spectrum of this stuff confirmed an obvious absorption peak at 270 nm, which verified the existence of  $\text{AgNO}_3$  (Fig. 1B). Therefore, part of  $\text{AgNO}_3$  could be deposited as Ag nanodendrites and the remaining helps to prevent oxidation of the generated nanodendrites.



**Figure 1.** (A) SEM image of Ag nanodendrites on Short-MWNTs-COOH. (B) UV-Vis image of Ag nanodendrites in water.

#### 3.2 Electrochemical behavior of the modified electrodes

EIS was carried out to indicate the interface properties of different modified electrodes in 0.1 M KCl solution containing  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (5.0 mM, 1:1). EIS analysis proved a semicircle in the higher frequency range and a linear in the lower frequency range. The former represented the electron transfer limited process and the latter was on behalf of a diffusion-limited process. Fig. 2A displays the EIS of Short-MWNTs-COOH/GCE (a), Ag nanodendrites/Short-MWNTs-COOH/GCE (b), Ag nanodendrites/GCE (c), and GCE (d). It can be easily found that Short-MWNTs-COOH/GCE had a very small semicircle diameter, which implied a very low electron transfer resistance ( $R_{ct}$ ). Due to the attendance of Short-MWNTs-COOH, the  $R_{ct}$  of Ag nanodendrites/ Short-MWNTs-COOH/GCE was lower than that of Ag nanodendrites/GCE. This phenomenon indicated that Ag nanodendrites and Short-MWNTs-COOH should be successfully modified on the surface of glassy carbon electrode.



**Figure 2.** (A) EIS of GCE (d), Ag nanodendrites/GCE (c), Short-MWNTs-COOH/GCE (a) and Ag nanodendrites/Short-MWNTs-COOH/GCE (b) in 0.1 M KCl solution containing  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (5.0 mM, 1:1). (B) CVs of GCE (c), Short-MWNTs-COOH/GCE (a), Ag nanodendrites/GCE (d) and Ag nanodendrites/Short-MWNTs-COOH/GCE (b) in 0.1 M KCl solution containing  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (1.0 mM, 1:1) at a scan rate of 50 mV/s.

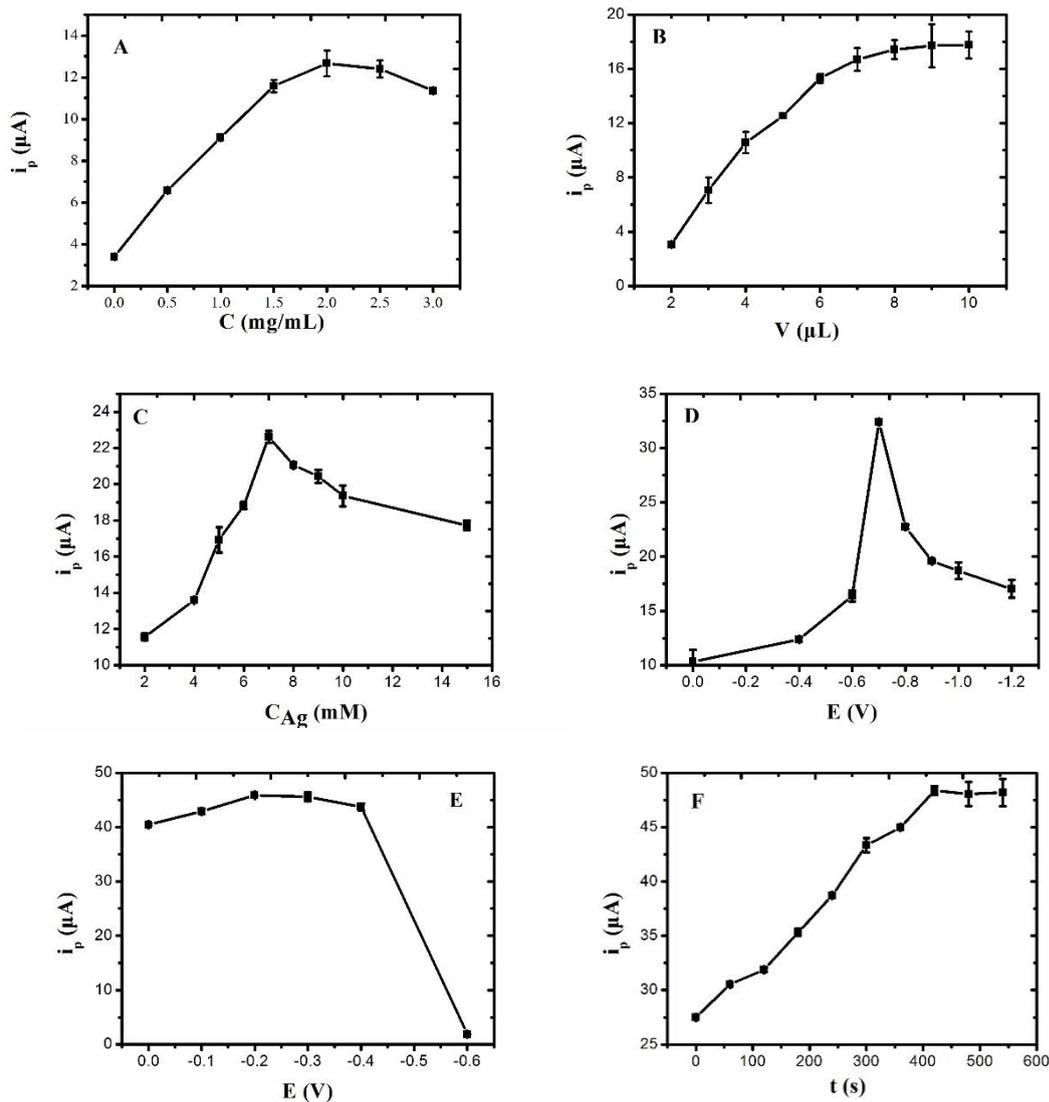
The CV image of different electrodes in 0.1 M KCl solution containing  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (1.0 mM, 1:1) at a scan rate of 50 mV/s is shown in Fig. 2B. As shown, Short-MWNTs-COOH/GCE displayed a pair of well-defined redox peaks compared to other electrodes. Considering the redox properties of Ag, the modified electrode of Ag nanodendrites/GCE showed an obvious peak current which was in accord with the previous report [13]. Compared to GCE, Short-MWNTs-COOH/GCE and Ag nanodendrites/GCE, the peak current of Ag nanodendrites/Short-MWNTs-COOH/GCE was increased significantly. This observation demonstrated that Short-MWNTs-COOH had been modified on GCE and Ag nanodendrites were successfully synthesized on the surface of electrodes. These results accord well with EIS analysis described before.

### 3.3 Optimization of the determination conditions

In order to achieve satisfactory results, a series of conditions were optimized. The influence of Short-MWNTs-COOH in various concentrations was investigated. Fig. 3A shows that the peak current of CAP was enhanced with increasing of Short-MWNTs-COOH content until 2 mg/mL. Analogously, 8  $\mu\text{L}$  was chosen as the best quantity to modify Short-MWNTs-COOH (Fig. 3B). It should be noted that too excess Short-MWNTs-COOH may lead to agglomeration and would block the electron transfer process.

Furthermore, it is important to improve the electrodeposition conditions of Ag nanodendrites. As shown in Fig. 3(C, D), when the concentration of  $\text{AgNO}_3$  achieved 7 mM, the electrodeposition potential of -0.7 V was attained, the electrodeposition time reached 10 s, and the peak current was maximized.

Moreover, the deposition conditions for determination of CAP are also discussed in Fig. 3 (E, F). These results indicated that the peak current approached an optimum value of -0.2 V for the deposition potential and under the electrodeposition time of 420 s.

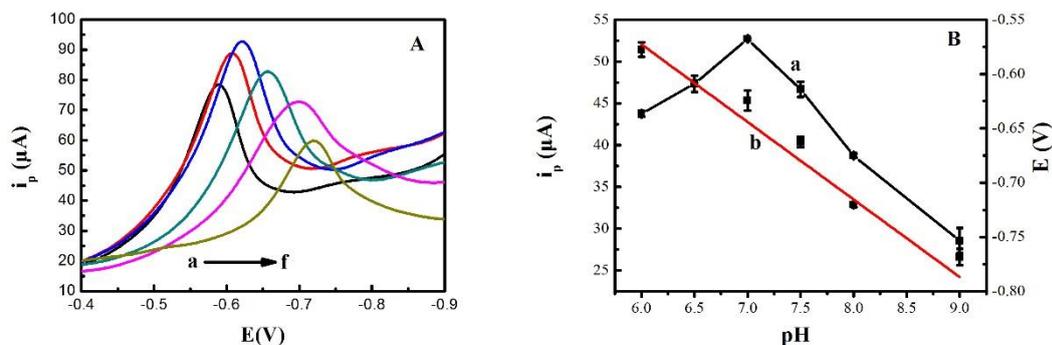


**Figure 3.** The influence for determination of CAP in different conditions: (A) the concentrations of Short-MWNTs-COOH, (B) the volume of Short-MWNTs-COOH, (C) the concentrations of Ag nanodendrites, (D) the electrodeposition potential of Ag nanodendrites, (E) the deposition potential of CAP and (F) the deposition time of CAP.

### 3.4 Optimization of pH

In addition to the above optimization conditions, pH of the electrolyte solution is also a vital factor for determination of CAP. In this experiment, pH from 6.0 to 9.0 was studied. From Fig. 4A and Fig. 4(B-a), it could be envisaged that the peak current was increased as pH value ranged from 6.0 to 7.0 and, then, decreased under pHs above 7.0. As a result, pH=7.0 was chosen as the best in this study.

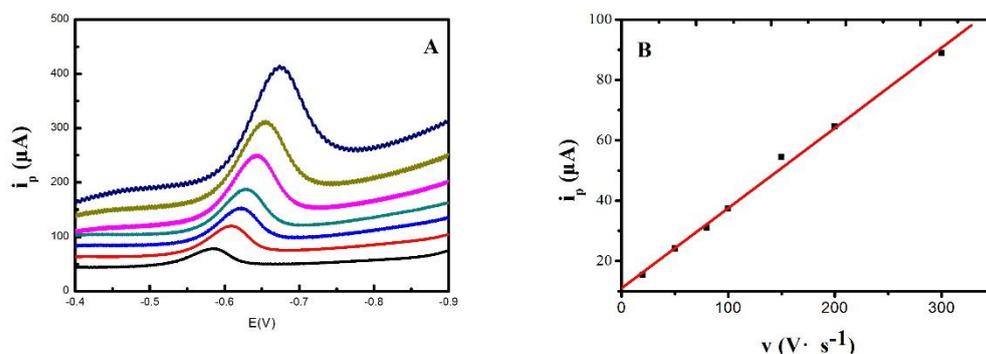
Fig. 4(B-b) exhibits the relationship between  $E$ (V) and pH according to the equation of  $E(\text{V}) = -0.05998\text{pH} - 0.2191$  ( $R^2 = 0.9908$ ). The slope of this equation was  $59.98 \text{ mV pH}^{-1}$  which is close to the theoretical value of  $57.6 \text{ mV pH}^{-1}$ . This result verified that electrons were equal to protons in this reaction.



**Figure 4.** (A) LSSV curves of 30.6  $\mu\text{M}$  CAP in different pH at a scan rate of 50 mV/s. (B) The plots for the relationships between peak current and pH (a), potential and pH (b).

### 3.5 Effect of scan rate

To further study the electrode reaction based on Ag nanodendrites/Short-MWNTs-COOH/GCE, different scan rates were investigated ranging from  $0.01 \text{ V}\cdot\text{s}^{-1}$  to  $0.3 \text{ V}\cdot\text{s}^{-1}$ . As shown in Fig. 5A, the peak current was enhanced gradually with the increase of scan rate. Fig. 5B displays a perfect linear relationship between the peak current and scan rate. The corresponding equation of  $i_p (\mu\text{A}) = 10.9217 + 0.2658 v (\text{V}\cdot\text{s}^{-1})$  ( $R^2 = 0.9976$ ) is derived, which implies an adsorption controlled process [16].

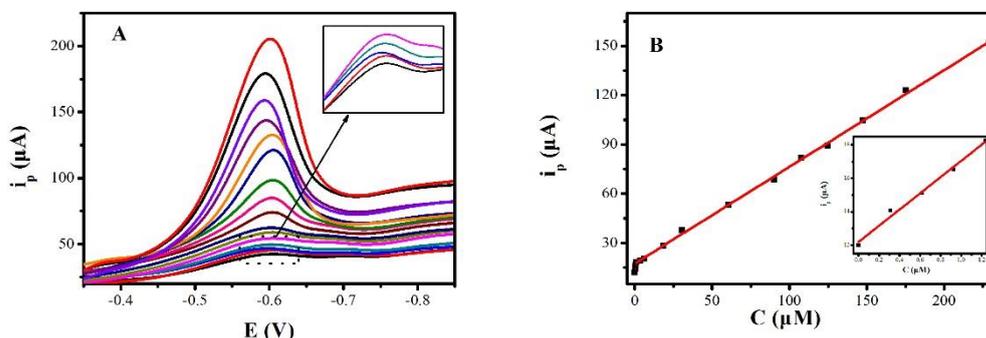


**Figure 5.** (A) LSSV curves of 30.6  $\mu\text{M}$  CAP in 0.2 M PB (pH=7.0) with different scan rates. (B) The linear relationships between the peak current and scan rates.

### 3.6 Electrochemical determination of CAP

Based on the optimized conditions, determination of CAP in PB (pH=7.0) was conducted by LSSV utilizing Ag nanodendrites/Short-MWNTs-COOH/GCE. Consistent with the literature, an obvious peak at  $-0.603\text{V}$  was observed, because the nitro group was reduced to hydroxylamine irreversibly [17]. Concentration of CAP was set in the range of  $0.3\text{--}229 \mu\text{M}$  (Fig. 6A) and the corresponding results confirmed a linear increase of the peak current with concentration (Fig. 6B). With the concentration of  $0.3\text{--}1.2 \mu\text{M}$ , the linear relationship between the reduction peak current and concentration obeyed the equation of  $i_p (\mu\text{A}) = 12.2080 + 4.9890 C_{\text{CAP}} (\mu\text{M})$ , ( $R^2 = 0.9868$ ). Analogously, the standard curve

equation for the concentration range of 1.2-229  $\mu\text{M}$  is  $i_p (\mu\text{A}) = 17.3900 + 0.5893 C_{\text{CAP}} (\mu\text{M})$ , ( $R^2 = 0.9989$ ). The detection limit (LOD,  $S/N=3$ ) for CAP was calculated as 0.049  $\mu\text{M}$ . Compared to other reported methods, the present route has a relatively lower detection limit, wider linear range, and satisfactory sensitivity (Table 1).



**Figure 6.** (A) The electrochemical determination for different concentration of CAP in the range of 0.3-229  $\mu\text{M}$ . The scan rate was 50 mV/s. (B) The relationships between the concentration and the response current of CAP in 0.3-1.2  $\mu\text{M}$  and 1.2-229  $\mu\text{M}$ , respectively.

**Table 1.** Comparison of different methods to determinate CAP

Electrodes	Method	Linear range ( $\mu\text{M}$ )	LOD ( $\mu\text{M}$ )	References
AuNPs/GO/GCE	i-t	1.5–2.95	0.25	[18]
AuNPs/N-G/GCE	DPV	2-80	0.59	[16]
3DRGO/GCE	DPV	1-330	0.15	[19]
SPAN/MoS <sub>2</sub> /CPE	DPV	0.1-1000	0.065	[20]
PANI–MoS <sub>2</sub> /CPE	DPV	0.1-100	0.069	[21]
rGO/AgNPs/aptamer/GCE	LSV	0.01–35	0.002	[22]
AgNPs/SF-GR/GCE	DPSV	0.2-20	0.01	[23]
AuNPs/BDD	SWV	5-35	5	[24]
Pt	DPV	2.4-92.9	—	[25]
Ag nanodendrites/Short-MWNTs-COOH/GCE	LSSV	0.3-229	0.049	This work

AuNPs: gold nanoparticles; GO: graphene oxide; N-G: nitrogen-doped graphene nanosheets; 3DRGO : three-dimensional reduced graphene oxide; SPAN: self-doped polyaniline; PANI: polyaniline; CPE: carbon paste electrode; rGO: reduced graphene oxide; SF-GR: sulfonated functionalized grapheme; BDD: boron doped diamond electrodes; Pt: platinum electrode.

### 3.7 Selectivity, repeatability and stability

In order to study the selectivity of this electrochemical sensor, tylosin, sodium sulfadiazine, norfloxacin, tetracycline, ascorbic acid, D-glucose, thiamphenicol, metronidazole and p-nitrophenol were investigated in 0.2 M PB (pH=7.0). The obtained results confirmed that compounds including nitro group had a great influence on the detection of CAP; whereas, the remaining compounds were almost

ineffective. The reproducibility was also studied by detection of CAP for ten modified electrodes and the RSD of about 4.55% was achieved. The stability was evaluated with one of the modified electrodes to determinate CAP for 10 times and the RSD of 7.58% was derived.

### 3.8 Real sample analysis

To analyze the reliability of the present electrochemical sensor based on Ag nanodendrites/Short-MWNTs-COOH/GCE, CAP was detected in some real samples involving honey, milk powder and eye drops. Due to no CAP detected in the samples, the standard addition method was applied to determine CAP in different concentrations. The test results of real samples were satisfactory as displayed in Table 2. In order to verify usefulness of the sensor, HPLC was applied as a reference method. Three spiked actual samples were simultaneously detected with HPLC and the present electrochemical sensor (Table 3). Findings showed that the values of CAP determined by the proposed sensor were very close to the data provided by HPLC. From the above results, the proposed electrochemical sensor could be applied for real samples with the advantages of cheap instrument, simple pre-processing and easy operation.

**Table 2.** The determination of CAP in real samples

Samples	Added ( $\mu\text{M}$ )	Found <sup>a</sup> ( $\mu\text{M}$ )	Recovery (%)	RSD (%)
Honey	0.62	0.64	103.21	0.49
	1.24	1.22	98.73	5.35
	6.18	6.47	104.63	3.80
Milk	6.18	6.45	104.37	7.37
	18.46	18.14	98.27	4.91
	30.64	29.85	97.42	4.33
Eye drops	0.62	0.60	96.87	3.76
	1.24	1.17	94.63	2.31
	6.18	6.30	101.94	3.70

<sup>a</sup> the average concentration of three individual measurements

**Table 3.** Comparison of the detection CAP obtained in real samples by electrochemistry and HPLC

Samples	1	2	3
This method ( $\mu\text{M}$ )	9.99	19.94	39.72
HPLC ( $\mu\text{M}$ )	10.0961	20.6906	40.4938
RSD(%)	-1.06	-3.76	-1.94

## 4. CONCLUSION

In a word, Ag nanoparticles were electrodeposited on Short-MWNTs-COOH in the presence of  $\text{NH}_3$  and the obtained electrochemical sensor based on Ag nanoparticle/Short-MWNTs-COOH/GCE showed high sensitivity to monitor CAP by LSSV and CV. The peak current proved a good linear relationship with concentration of CAP from 0.3 to 229  $\mu\text{M}$ . This new protocol can be recommended for

determination of CAP in real samples with satisfactory results, which handles high electrocatalytic activity, sensitivity, reproducibility, and low cost.

#### ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundations of China (21575067).

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