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Catalase Immobilized ZnO Nanorod with β-cyclodextrin Functionalization for Electrochemical Determination of Forchlorfenuron

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In this communication, we demonstrated a forchlorfenuron (FF) electrochemical biosensor based on a catalase immobilized ZnO nanorod with β-cyclodextrin functionalization (CA-β-CD-ZnO). CA was immobilized on the β-CD functionalized ZnO rods. The prepared CA-β-CD-ZnO was highly sensitive to the electrochemical reduction of H_2O_2. After introduction of FF into the H_2O_2 electrochemical detection system, the current change had a linear relationship with the FF concentration. Investigation showed the CA-β-CD-ZnO could be used for detecting FF in the concentration range between 0.005 to 2 μM with a low detection limit of 0.002 μM. Moreover, the CA-β-CD-ZnO was successfully demonstrated for FF detection in fruit samples.

Keywords: Catalase; ZnO rod; β-cyclodextrin; Forchlorfenuron; Electrochemical sensor

1. INTRODUCTION

1-(2-chloropyridin-4-yl)-3-phenylurea, also known as forchlorfenuron (FF) is a plant hormone which controls plant growth. In current agriculture industry, FF was widely used for plant cell division, which could enhance plant organ formation as well as molecule synthesis [1, 2]. Especially in the fruit industrial, FF was used for promoting the fruit production [3]. Therefore, it is possible the residues of agriculture waste could pass the FF into human body. The maximum dosage of FF for human intake should be less than 200 nM in any food [4]. Studies showed the long-term contact FF could result mild emphysema and protein metabolism disorder. Therefore, the content of the FF in food residue should be monitored by a reliable method [5]. So far, many different approaches were developed for FF

determination, including UV-vis spectroscopy detection [6], mass spectrometer [7]. These methods have been demonstrated for successful detection of FF. However, they still suffer some drawbacks, such as high cost, sophistication of the apparatus and skilled operation technician requirement. On the other hand, biosensing method shows a quick, simple and low-cost performance because it only requires simple sample pretreatment, high sensitivity and wide detection range [8-22]. The inhibition effect caused by enzymes is a steam of developing bionsensing method [23, 24]. Catalase (CA) is an excellent enzyme could be used for developing inhibition effect based bionsensor [25-28]. CA is a biological catalyst, which could effectively catalyze biological reaction in different conditions. It also has other advantages such as low-cost, excellent stability and high activity. Therefore, the CA is an ideal candidate for electrochemical determining its inhibitors.

ZnO is a well-studied material commonly used for electrode construction. Its nanostructures have been found owing high surface area and electrochemical properties. Recent studies show the the ZnO nanostructure could be used for electrochemical sensor develop [29-34]. For example, Wang and co-workers demonstrated a multiwalled-carbon nanotube-ZnO/chitosan nanocomposite for norepinephrine and serotonin electrochemical detection [35]. Manjunath and co-workers fabricated a dopamine electrochemical sensor based on ZnO nanorods [36]. Moreover, Patra and co-workers demonstrated a clinical calcitonin biosensor based on imprinted ZnO nanostructures. Meanwhile, β-Cyclodextrin (β-CD) is a cyclic oligosaccharide, which structurally has a hydrophobic inner cavity with a hydrophilic exterior. This unique structure offers the β-CD owing a host–guest inclusion complexes, which could be used for recognizing small molecules. Till now, many biosensors have been developed based on its unique host–guest property [37-40].

In this contribution, we use β-CD as functionalization molecules for chemically synthesized ZnO rod surface modification. CA was then immobilized onto the β-CD-ZnO, and the CA-β-CD-ZnO was then used as an electrode surface modifier for glassy carbon electrode (GCE) modification. The CA-β-CD-ZnO/GCE was used for FF electrochemical determination. Figure 1 displays the electrode fabrication process with its detection procedure. Due to the effective catalytic performance of the CA, H_2O_2 could be simply reduced in the electrochemical system. However, this catalytic reduction process was inhibited by the presence of FF, which represented as a lower current response. The quantitative analysis of FF concentration could be achieved by comparing the current signal decreasing.

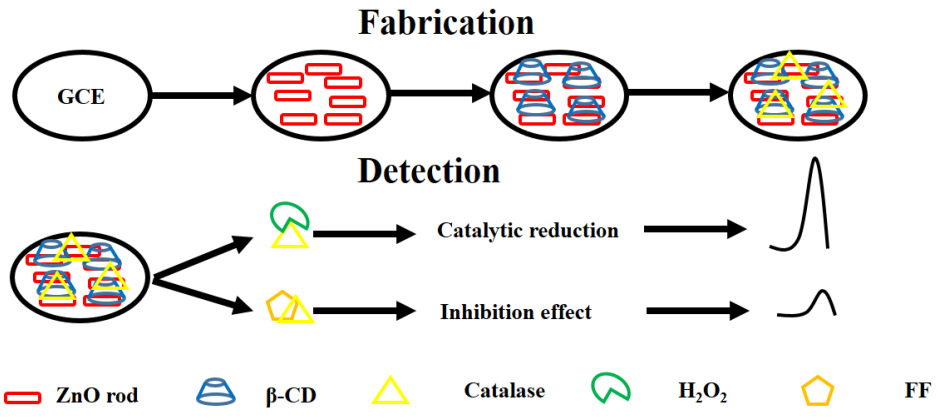

Figure 1. Schematic diagram of CA-β-CD-ZnO fabrication and FF detection mechanism.

2. EXPERIMENTS

2.1 Chemicals and materials

Catalase (E.C. 1.11.1.6), thiourea, β-CD, forchlorfenuron, $NH_3 \cdot H_2O$, H_2O_2, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, hydrazine solution (25% in water) was purchased from Sigma. 0.1 M forchlorfenuron was prepared in ethanol as a stock solution. Phosphate buffer solution was prepared by mixing monosodium phosphate and disodium phosphate. The fruit (rock melon, kiwi and apple) were purchased in local fruit shop as real samples.

2.2 Synthesis of CA-β-CD-ZnO rods

CA-β-CD-ZnO was synthesized using following procedure: 2 mL hydrazine solution (0.1 M) was drop by drop added into 20 mL $Zn(NO_3)_2 \cdot 6H_2O$ (0.05 M) under magnetic stirring. ZnO rods was collected by centrifugation followed by water wash. Then, ZnO rods were dispersed into 20 mL water by 1 h sonication and adjusted pH to 10. 1 mL β-CD (0.5 M) was added into above dispersion followed by additional 1 h sonication. The dispersion was centrifuged and washed by water twice. Solid sample was collected by drying the sediment under oven for 6 h. Immobilization of catalase on the β-CD-ZnO was through adsorption. Briefly, 0.1 mL of catalase (10 mg/mL) solution was added into 0.1 mL β-CD-ZnO dispersion (0.5 mg/mL). CA-β-CD-ZnO was achieved by sonicated above dispersion for a half hour for the adsorption process.

2.3 Characterization

The morphology and structure of the samples were characterized by a field emission scanning electron microscopy (ZEISS, SUPRA 55). The electrochemical measurements were carried out using a CHI 660 electrochemical workingstation. A conventional three-electrode system with a platinum electrode as the auxiliary electrode and an Ag/AgCl (3M) as the reference electrode. GCE was used as working electrode.

2.4 Electrochemical determination of forchlorfenuron

All electrochemical measurements were carried out at a 10 mL glass cell. N_2 saturated PBS with pH 7 was used as electrolyte. Flow injection method was used for FF measurement (flow rate: 1 mL/min). Different concentrations of FF were introduced into the PBS (containing 1 mM H_2O_2). The catalase inhibition performance (%I) can be calculated as follow: $\%I = (I_i - I_F)/I_i * 100$. Where I_i and I_F are the current responses of no forchlorfenuron and with forchlorfenuron, respectively.

2.5 Fruit sample preparation

Fruit sample preparation was according to following procedure: 500 g fruit was peeled and chopped into slurry. The slurry was added into chloroform and centrifuged for removal of solid part.

After evaporation of chloroform, the residue sample was dispersed into 10 mL ethanol for electrochemical analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of CA-β-CD-ZnO

In this work, ZnO rods and β-CD were used for adsorbing CA. β-CD functionalized ZnO rods is a biocompatible material, which provides an excellent condition for catalase immobilization. Figure 2 A shows the SEM image of the β-CD functionalized ZnO rods. It can be seen that the ZnO rods have an average diameter of 300 nm. The β-CD cannot be directly observed using SEM analysis. However, the dispersibility of the ZnO rod improved after β-CD functionalization. A milky suspension of β-CD-ZnO could maintain a stable state over a month. From the SEM, no clear aggregation was observed. The morphology of CA immobilized β-CD-ZnO was also characterized using SEM. As shown in Figure 2B, the CA-β-CD-ZnO shows a similar morphology compared with that of β-CD-ZnO, indicating the CA was well dispersed on the β-CD-ZnO without aggregation. The successful immobilization process was confirmed by UV-vis spectroscopy analysis. The pure CA exhibits a characteristic absorption peak at 272 nm. After adsorption process, we centrifuged the mixture and collected the supernatant. Almost no CA absorption peak observed in the spectrum, indicating all CA molecules were adsorbed on the β-CD-ZnO.

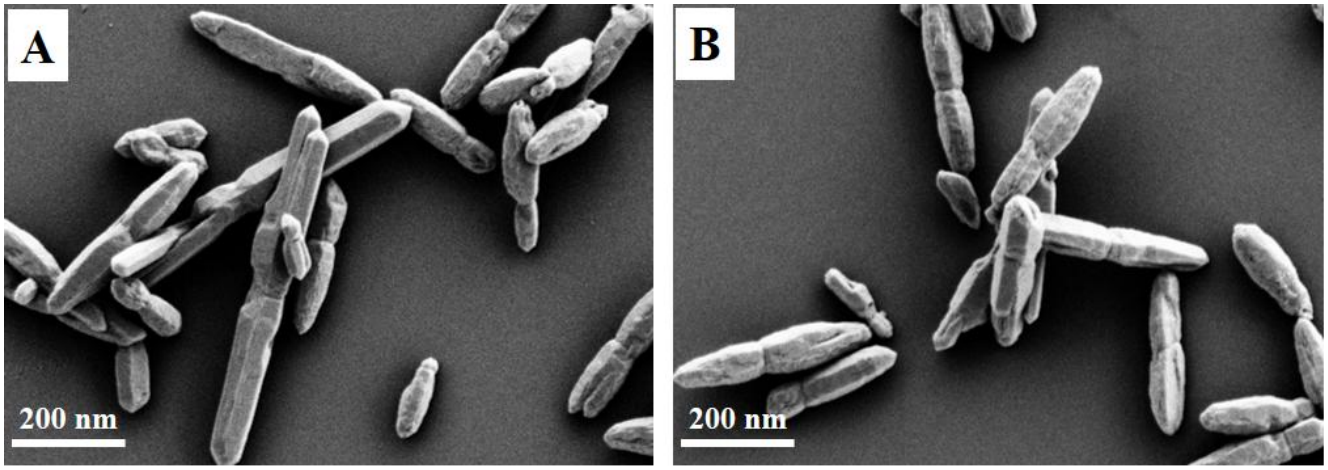

Figure 2. SEM images of (A) β-CD-ZnO and (B) CA-β-CD-ZnO.

3.2 Electrochemical behaviour of CA-β-CD-ZnO modified GCE

Figure 3A shows the CV profiles of bare GCE, CA/GCE, β-CD-ZnO/GCE and CA-β-CD-ZnO/GCE in the PBS solution. As shown in the figure, bare GCE and β-CD-ZnO/GCE shows no signals in the scan range, indicating both electrodes did not react with any species during the scan. In

contrast, CA/GCE and CA-β-CD-ZnO/GCE shows a clear pair of redox peaks in the scan range, which can be ascribed to the Cat-Fe(III)/Cat-Fe(IV) redox couple by CA. However, the peak current of CA/GCE is less than that of CA-β-CD-ZnO/GCE, suggesting the β-CD-ZnO accelerate the electron transfer between the CA and GCE surface. Moreover, the CA-β-CD-ZnO/GCE shows an excellent stability while the CA/GCE decreased the current after each scan. Therefore, the β-CD-ZnO can be used as an excellent substrate for CA immobilization and facilitates the electrocatalytic performance.

Catalase could effectively electrocatalytic reduce H_2O_2. Figure 3B shows the CV profiles of CA-β-CD-ZnO/GCE with or without 0.1 mM H_2O_2. It can be clearly seen that the peak current showed dramatically increasing when the presence of H_2O_2, suggesting the catalase could effectively reduce the H_2O_2. The following equation was used for explaining the H_2O_2 reduction.

$$H_2O_2 + \text{CA-Fe(III)} \rightarrow H_2O + \text{CA-Fe(IV)=O}$$

$$H_2O_2 + \text{CA-Fe(IV)} \rightarrow \text{O=}H_2O + O_2 + \text{CA-Fe(III)}$$

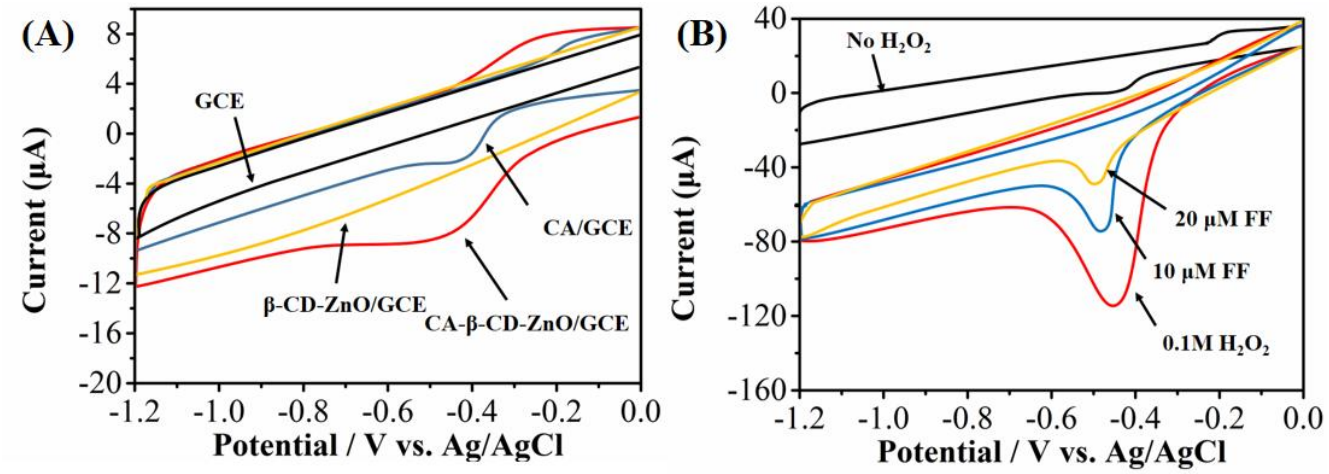

Figure 3. (A) CV profiles of bare GCE, CA/GCE, β-CD-ZnO/GCE and CA-β-CD-ZnO/GCE in the PBS solution. (B) CV profiles of CA-β-CD-ZnO/GCE towards 0.1 mM H_2O_2 with different concentrations of FF.

Figure 3B also presents the inhibitory effect of FF on the H_2O_2 reduction signal. It can be seen that different concentrations of FF introduced into the system could effectively lower the H_2O_2 reduction current. Moreover, the current response decreased when the concentration of FF increasing. Based on these observations, it can be concluded that the presence of FF could inactivation of the catalytic sites of the catalase, which lower the H_2O_2 reduction performance. We found the decreasing of the current signal had a linear relationship to the concentration of the FF in the system.

We then optimized several parameters could affect the detection performance of CA-β-CD-ZnO/GCE towards FF, including the ratio between CA and β-CD-ZnO, the pH condition, the electrolyte type, detection potential and substrate concentration.

The inhibition performance was enhanced when the CA to β-CD-ZnO ratio increased from 1:1 to 5:1. Further increasing of CA shows a stable performance, indicating the β-CD-ZnO could adsorb 5-fold of CA. Therefore, the optimum ratio between CA and β-CD-ZnO ratio was chosen as 5:1.

pH condition was also a critical parameter for inhibition result. We tested the inhibition degree using CA-β-CD-ZnO/GCE for 0.05 mM FF. The inhibition is degree increased when the pH value from 3 to 7 and reached the maximum value at 7. Further increasing pH showed a decreasing of inhibition degree. A similar results were reported by other's work. Therefore, pH 7 was chosen in this study.

The inhibition degree can be greatly affected by the applied potential due to the different electroactivity of H_2O_2 at different potential. Our study demonstrated that the inhibition degree of CA-β-CD-ZnO/GCE towards 0.05 mM FF increased from —0.1 to —0.45 V. A decreasing of the current response was observed when more negative potential was applied. Therefore, the applied potential was fixed at —0.45 V.

The effect of concentration of H_2O_2 with inhibition degree was studied as well. We estimated the detection limit of the CA-β-CD-ZnO/GCE using different H_2O_2 concentrations as substrate. A higher H_2O_2 concentration could result in a decreasing of inhibition effect of the CA. A lower H_2O_2 concentration only can provide a weak response. After optimization, the concentration of H_2O_2 was chosen as 0.1 mM in this study.

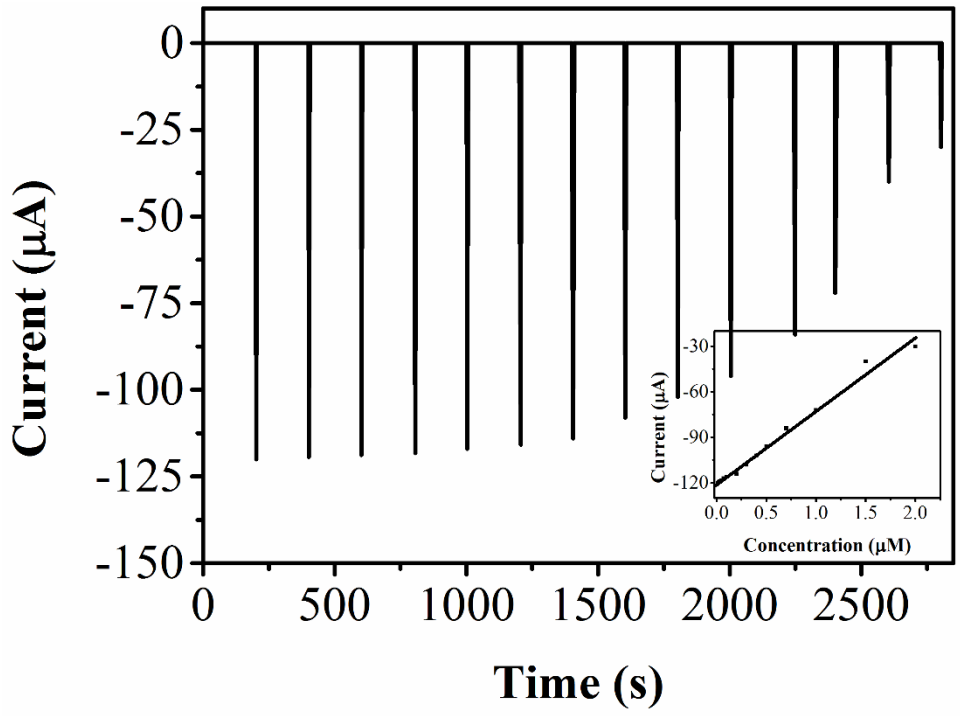

Figure 4. Amperometric detection of different FF concentration using CA-β-CD-ZnO/GCE. Inset: calibration curve between the FF concentrations and current responses.

After optimization, the detection range of FF using CA-β-CD-ZnO/GCE was studied. Figure 4 shows the amperometric curves of the CA-β-CD-ZnO/GCE toward a succession of FF addition in the 0.1 mM H_2O_2. It can be clearly seen that the current response was decreased when the FF

concentration increasing. The current tented to a stable state when a large amount of FF presented in the system, indicating the binding sites between CA and FF reached an equilibrium condition. A linear relationship was observed between the concentrations of FF and current response from 0.005 to 2 μM. The regression equation could be expressed as: I (μA) = 0.4847C (nM) ―120.618 (R^2 = 0.989). The detection limit of the CA-β-CD-ZnO/GCE towards FF detection can be estimated as 0.002 μM. Our proposed FF sensor showed a wider detection linear range and lower detection limit compared with many other existing reports [41-50]. The reason that our proposed electrochemical sensor had wider detection range with lower detection limit can be ascribed to the following reasons: Firstly, the capacity of β-CD to form host-guest complexes with resulting in more FF molecules are attracted on the electrode surface [51]. Secondary, the nano-sized ZnO rods provide high specific surface area for electrochemical reaction taken place, which highly enhanced the current signal when adding FF [8, 34, 52-54]. Moreover, the synergistic effect of β-CD and ZnO nanorods provide a superior interface for performing the sensitive electrochemical measurement of FF.

The selectivity performance of CA-β-CD-ZnO/GCE towards FF detection was then studied. Results indicate the detection performance did not affect by the 200-fold of glucose, ascorbic acid, uric acid, sucrose, glycine, citric acid, K^+, Na^+ and Ca^{2+}. The good selectivity of the CA-β-CD-ZnO/GCE provides a reliable approach for analyzing FF in real applications.

The stability of the CA-β-CD-ZnO/GCE was tested by ten times of detection of 10 μM FF. A decreasing of 7 % of current was observed. The reproducibility of the CA-β-CD-ZnO/GCE was tested by the ten individually fabricated sensor. A RSD of 5.44% was observed. Based on these results, our prosed CA-β-CD-ZnO/GCE exhibited a reliable performance towards FF detection. The real sample test was performed using apple, pineapple and kiwi fruit. Table 1 shows the measurement performance and compared with HPLC results. The results indicate the CA-β-CD-ZnO/GCE exhibited a better performance than that of the HPLC, indicating our proposed biosensor could be successfully used for FF detection in real samples.

Table 1. Real sample test results using CA-β-CD-ZnO/GCE and HPLC.

Sample	Spiked (μM)	Found (μM)		Recovery (%)
		CA-β-CD-ZnO/GCE	HPLC	
Apple	5	4.89	5.13	97.8
Rock melon	10	10.21	10.29	102.1
Kiwi fruit	15	14.99	15.22	99.9

4. CONCLUSIONS

In this work, we synthesized ZnO nanorods via a chemical method followed with a surface functionalization of β-CD. The β-CD-ZnO was then used for CA immobilization. The CA-β-CD-ZnO was the used as an electrode surface modifier for constructing a FF biosensor. The inhibition degree of the CA-β-CD-ZnO was studied in detail. Results showed that our proposed CA-β-CD-ZnO/GCE

biosensor is highly sensitive for FF detection. Moreover, the real sample test result indicated the CA-β-CD-ZnO/GCE could be successfully used for FF determination in fruit samples.

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