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Supramolecular imprinted sensor for carbofuran detection based on a functionalized multiwalled carbon nanotube-supported Pd-Ir composite and methylene blue as catalyst

Shuhuai Li[a,b,*], Guihao Yin[a,b], Xuejin Wu[a,b], Chunhua Liu[a,b], Jinhui Luo[a,b,*]

[a] Analysis and Test Center of Chinese Academy of Tropical Agricultural Sciences, Haikou 571101, China
[b] Hainan Provincial Key Laboratory of Quality and Safety for Tropical Fruits and Vegetables, Haikou 571101, China

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ABSTRACT

A novel supramolecular imprinted electrochemical sensor was developed for carbofuran (CBF) determination based on a multiwalled carbon nanotube-supported Pd-Ir nanocomposite catalyst (MWCNT/Pd-Ir) with methylene blue (MB) signal amplification. First, MWCNT/Pd-Ir composite nanoparticles were synthesized and used to modify the surface of a glassy carbon electrode; then, a molecular imprinted polymer for CBF was prepared by electropolymerization, with MB-doped *o*-phenylenediamine as the functional monomer and a 4-tert-butylcalix[8]arene-CBF (4TB[8]A-CBF) supramolecular complex as the template. The electrical signals were controlled though the elution and re-adsorption of CBF. Due to the double catalysis by the MWCNT/Pd-Ir and MB, the current intensity for CBF was obviously amplified. Additionally, because of the double recognition by the 4TB[8]A and MIP, the sensors showed outstanding CBF identification properties. The method was applied to detect CBF in agricultural products, and the satisfactory results were obtained.

1. Introduction

Carbofuran (CBF) [1] is one of the most toxic carbamate pesticides. Although it was used extensively worldwide in agricultural applications, it was severely restricted in many countries after it was found to be persistent and bio-toxic. However, because it still presents a major threat to human health and the ecosystem, it has become especially important to monitor the CBF content in agricultural products and the environment. There are numerous ways to detect CBF, with high performance liquid chromatography (HPLC) [2] and HPLC-mass spectrometry (HPLC-MS) as the leading methods [3,4]. While accurate, these methods can be laborious and expensive, and require time-consuming and tedious pretreatments of the samples. Besides that, electrochemical sensors have also been used in detecting CBF [5–7]. Jeyapragasam and Saraswathi [8] report a square wave voltammetric biosensor for the determination of CBF using an acetylcholinesterase enzyme immobilized iron oxid-chitosan nanocomposite film. The biosensor could detect carbofuran as low as 3.6×10^{-9} mol/L. But, the selectivity of these sensors needs to be further improved. So, new methods which are facile and demonstrate good selectivity, high sensitivity, and simple pre-processing would be desirable.

The molecular imprinting technique (MIT) [9] is used to prepare molecular imprinted polymers (MIPs) with recognition sites that have predetermined selectivity for given molecules. It has been widely applied in sensors for environmental monitoring [10], pesticide residue analysis [11], bioanalysis [12], and food detection [13] due to its dominant recognition and selectivity. Tan [5] developed a molecularly imprinted electrochemical sensor based on glassy carbon electrode decorated by reduced graphene oxide and gold nanoparticles for the detection of carbofuran with a detection limit of 2.0×10^{-8} mol/L. In this case however, sensor exhibited good selectivity for CBF but the detection sensitivity wasn't ideal. In order to meet the requirements of complex matrix samples, the selective recognition of MIP need to enhance efforts, due to the relatively limited recognition sites in the in the MIPs and their imprinted capacities [14]. Other recognition technologies such as supramolecular chemistry and nanometer catalyst materials have been introduced to enhance sensitivity and selectivity in recent years.

Supramolecular chemistry [15] involves the self-assembly of small molecular units into larger molecular constructs via non-

* Corresponding authors at: Analysis and Test Center of Chinese Academy of Tropical Agricultural Sciences, Haikou 571101, China.
E-mail addresses: happylishuhuai@163.com (S. Li), luocatas@21cn.com (J. Luo).

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covalent bonding. Such assemblies can offer the selective recognition of a template molecule due to the host-guest molecular recognition principle. To date, cyclodextrins [16], crown ethers [17], and porphyrins [18] have been studied most often as host molecules. As third-generation supramolecules, calixarenes [19] have unique structures such as controlled vacuum widths and can be easily derivatized, and thus offer advantages in host-guest molecular recognition. However, host-guest molecular recognition based on calixarene derivatives has rarely been used in MIP sensors.

In terms of improving the sensitivity of MIP sensors, strategies have focused on nanometer-sized materials to amplify the detected signal. Among the most popular have been metal nanoparticles [20], carbon nanotubes [21], semiconducting quantum dots [22], and grapheme [23]. Of these, metal nanoparticles have high specific surface areas and very active surface atoms; they are very attractive catalysts for electrochemical reactions, compared to bulk catalysts. For example, catalytically active gold [24], silver [25], and platinum [26] nanoparticles have found promising application in MIP sensors. Of the various nanometer-sized materials, multiwalled carbon nanotubes (MWCNTs) [27] exhibit many extraordinary properties, such as special structures and outstanding mechanical and unique electronic properties. The development of a composite MWCNT-supported metal nanoparticle catalyst would have great potential for increasing sensor sensitivity. Another strategy for enhancing the sensitivity of an MIP sensor could involve the incorporation of the electroactive substance, methylene blue (MB) [28]. This phenothiazine species, which has superior reversible redox activity, would exhibit excellent electrocatalytic activity in a conductive substrate. To our knowledge, however, a MWCNT-supported Pd-Ir nanocomposite catalyst (MWCNT/Pd-Ir) together with MB for an MIP sensor has not been reported.

In this paper, a glassy carbon electrode (GCE) which was doubly modified with MWCNT/Pd-Ir and the MB-doped MIP was used to prepare a novel sensor for CBF detection. First, 4-tert-butylcalix[8]arene (4TB[8]A)-CBF (4TB[8]A-CBF) supramolecular inclusions were prepared via self-assembly. Then, the MB-doped MIP was prepared via electropolymerization, using MB-doped *o*-phenylenediamine as a functional monomer and the 4TB[8]A-CBF supramolecular inclusions as the template molecules. Due to the electroactivity of CBF, it was designed as a switch to control the current intensity by its elution and adsorption in the MIP. Both the cavity identification of the introduced 4TB[8]A and the imprinted sites of the MIP provided an increased number of CBF recognition sites, ultimately resulting in an MIP sensor which exhibited better selectivity. Furthermore, the double catalytic effect of the MWCNT/Pd-Ir and MB increased the current intensity of the sensor. The construction of the MIP sensor is illustrated in Fig. 1.

2. Experimental

2.1. Reagents and apparatus

CBF standards, MWCNT (Inside: 20–50 nm, outside diameters: 50–100 nm, length: 1–3 μm), palladium chloride ($PdCl_2$), *o*-phenylenediamine, methylene blue and ammonium hexachloroiridate ($H_8Cl_6IrN_2$) were obtained from Aladdin Industrial Corp. (Shanghai, China). 4-tert-Butylcalix[8]arene was obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). All reagents were analytical grade. All aqueous solutions were prepared with doubly distilled water.

Electrochemical measurements were performed with a standard three-electrode workstation (CHI660E, Shanghai Chenhua Instrument Co. Ltd., Shanghai, China). A KCl-saturated Ag/AgCl electrode was the reference electrode, a platinum wire was the auxiliary electrode, and the MIP-modified GCE was the working electrode.

2.2. Preparation of 4TB [8]A-CBF inclusions

Inclusions were prepared by self-assembly. A mixed solution of CBF (1×10^{-5} mol/L) and 4TB[8]A (diluted with phosphate-buffered saline (PBS) solution, 0.05 mol/L, pH = 7.8) was blended for 30 min by ultrasound and allowed to stand overnight at 4 °C. Then, the solution was cooled, filtered, and washed with absolute ethyl alcohol, to afford the 4TB[8]A-CBF inclusions. Then the purity of 4TB[8]A-CBF inclusions were obtained by recrystallization and dried in a vacuum oven at 60 °C for 2 hours.

2.3. Preparation of MWCNT/Pd-Ir nanocomposite-modified electrodes

To prepare the electrode surface, the GCE was ultrasonically cleaned in succession with acetone, ethanol, and deionized water for 3 min. Then, a few drops of a 0.5% Nafion^{TM} solution containing 0.5 mg/mL MWCNTs were spread on the surface of the GCE, and allowed to dry in air. The MWCNT-modified GCE was subjected to electroreduction in a mixed electrolyte solution of 0.01 mol/L HCl, 0.001 mol/L $H_8Cl_6IrN_2$, and 0.001 mol/L $PdCl_2$ under nitrogen atmosphere, to form the Pd-Ir layer [29]. The CV potential range was 0.6 to −1.5 V over 20 cycles, at a scan rate of 50 mV. Then, the MWCNT/Pd-Ir nanocomposite-modified electrodes were obtained.

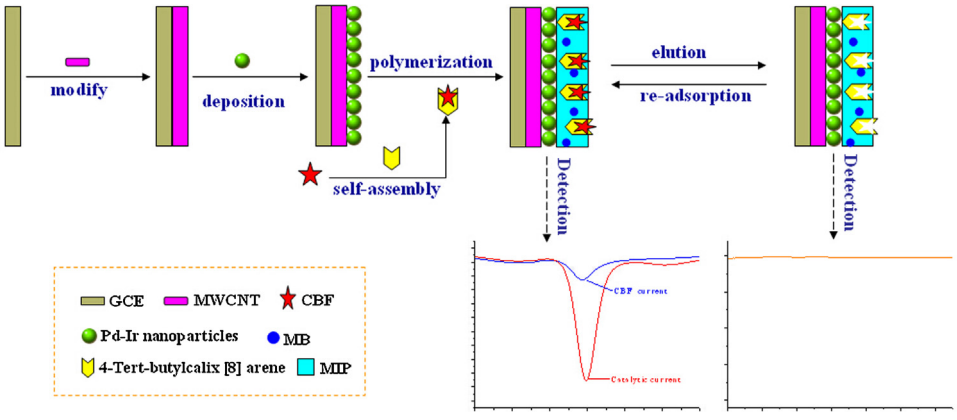

Fig. 1. The procedure to construct sensor and determine of CBF.