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Electrochemical Sensors with Antifouling Properties for Sensitive Detection of Isoproturon Based on Glassy Carbon Electrode Modified with Nafion Membrane

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An ultra-high antifouling electrochemical sensor has been established and described for determination of isoproturon (ISO) in the practical complex sample owing to its chemical stability. The complexity of practical sample severely influences the reliability and stability of sensors for ISO detection. Therefore, design an effective antifouling electrode is necessary. Glassy carbon electrode (GCE) modified with Nafion membrane was applied to monitor ISO via square wave voltammetry (SWV), showing great promising practical application for pesticide residue detection. The proposed sensor can sensitively detect trace levels of ISO with a linearity ranging from 0.09 to 20.00 μM, with a limit of detection (LOD) of 0.03 μM (S/N=3), which was superior to that of nanomaterial modified ISO electrochemical sensors. The high sensitivity is mainly attributed to the specifically electrocatalytic activity towards ISO catalyzed by hydrogen radical derived from the sulfonic group of Nafion. Additionally, the sensor for detecting ISO in actual test specimens like tomato, lettuce and water in rice field shows ultra-high stability and repeatability together with reproducibility.

Keywords: Real sample; Isoproturon; Antifouling; Square wave voltammetry; Electrochemical sensor; Ultra-stability

1. INTRODUCTION

Isoproturon (ISO), one of the important herbicides of phenylurea family, has been widely applied for controlling weeds growth in the field of crops. Although the largescale application of ISO brings foison of food supplies, the residues of ISO readily accumulated in soils, ground waters, and crops have become a serious contaminant in ecosystems[1]. ISO is proved to induce toxicity, especially aggravating damage of low temperature stress, to the food crop wheat [2,3]. ISO, together with the degradation metabolites, has also been suspected to be carcinogenic on human being and animals [4]. ISO has been banned in the European Union and several countries due to its poisoning effect, with strictly restricted maximum residue limit (MRL) within food resource. Therefore, developing the reliable and sensitive techniques is urgently needed to screen whether its existence within food resource satisfies the increasingly demanding pollution restriction. However, precise and reliable detection of agricultural residues in water, fruits and vegetables is not an easy work owing to the matrix effect.

Traditional methods used to analyze agricultural residues, particularly for ISO, have been commonly developed on the basis of the chromatography [5-9]. These methods are characterized with low limit of detection (LOD), favorable reproducibility, and great sensitivity, but are highly demand of costly equipment, skilled operator, and tedious sample clean-up steps, which limits its further in-situ analysis. Recently, a type of emerging technique i.e., electrochemical sensor has been developed for screening of pesticides in food samples [10-13]. Compared with additional approaches such as chromatography and spectroscopy, electrochemical sensor has many merits such as high efficiency, simple portability, and excellent sensitivity, and these meet requirements for rapid assessment of food safety. In electrochemical sensing field, electrode material exerts an important part during high-performance sensor construction [14]. Therefore, great attention is paid to the development of diverse functional nanomaterials in recent years[15], like quantum dots [12,18], metal nanoparticles [16,17], and carbon-based nanomaterials[19,20] and two-dimensional materials[21] to design advanced sensors. By virtue of its high surface area, superb conductivity and catalytic ability, nanomaterials can substantially improve analysis performance, amplify signal for detection, and stabilize sensing interface or identification probe [14]. However, considerable progress has not been made in ISO detection via electrochemical sensor based on nanomaterials[22,23]. These nanomaterial-based electrodes usually suffer from strong fouling effect, resulting in poor electrochemical stability, which greatly restricts the practical application for ISO detection. A fundamental reason is that ISO has poor electrochemical activity towards nanomaterials owing to ISO stable ring structure. In addition, nanomaterials have strong adsorption ability towards ISO due to the high surface area, resulting in strong fouling effect toward electrode. Consequently, it is still highly desirable to develop the functional electrode material that has a great electrocatalysis and antifouling effect towards ISO is still of highly desirable.

Nafion, developed by E. I. DuPont Company, is a perfluorosulfonated polymer composed of one perfluorocarbon backbone along with various vinylether side chains that are ended with the sulfonic acid groups [24]. Owing to its unique properties such as high stability, good solubility, and ionic conductivity, Nafion has been widely employed as a proton exchange membrane in fuel cells[25], metal-ion recovery[26], water electrolysis[27] and batteries[28]. In addition, Nafion is a type of superacid catalyst commonly used in many organic reactions because its surface acidity is parallel to the 100% sulfuric acid [29,30]. Typically, fluorocarbon has chemical inertness and a great acid strength, rendering Nafion the promising candidate of solid acid catalyst [31,32].

Similarly, the antifouling composite films constituted by the Nafion- or graphene oxide (GO)-modified glassy carbon electrode (GCE) and poly(3,4-ethylenedioxythiophene) (GO-PEDOT) were chosen, respectively, to prepare ultrasensitive sensor for quantifying paraquat or adenosine triphosphate (ATP) [33,34]. Also, the carbon ceramic electrode modified with Nafion by consideration of its antifouling effect increases the reproducibility of detection for l-Cysteine [35]. Nafion-doped GCE shows a good stability, reproducibility and strong ability against electrode fouling accumulating potential [36-38].However, the utilization of Nafion for the detection of pesticide residue in the fruit and vegetables sensing has not been reported.

Inspired by the aforementioned work, we herein developed an electrochemical sensor based on a commercially available polymer Nafion according to the easy facile drop-coating approach, and our as-prepared sensor was first used in ISO detection by means of square wave voltammetry (SWV). A linearity relationship between the electrochemical response detected by Nafion-based sensor and ISO concentration ranging from 0.09 to 20.00 μM, and the limit of detection (LOD) can be decreased to 0.03 μM. Moreover, the sensor Show ultra-high electrochemical stability, which was ascribed to the antifouling ability of Nafion. In addition, the feasibility of practical application was evaluated via analyzing various spiked actual test specimens, such as lettuce, tomato, water in rice field, and satisfactory recovery was obtained, revealing it is reliable for remarkable performance in practical uses.

2. EXPERIMENT

2.1 Chemicals and Regents

Isoproturon (99.00% of purity), carbendazim (97% of purity), carbary (98% of purity), vitamin C (≥99.7% of purity), KCl (99.5% of purity), potassium ferrocyanide ($K_4[Fe(CN)_6]$, 99.0% of purity), potassium ferricyanide ($K_3Fe(CN)_6$, ≥ 99.5% of purity), N-N dimethylformamide (99.5% of purity) were provided by Aladdin reagent Co. Ltd. Nafion D521 dispersion (5% w/w in water and 1-propanol) was obtain from Alfa Aesar Co. Ltd. The ISO stock solution with concentration of 0.01000 $mol\cdot L^{-1}$ was dissolved in N-N dimethylformamide before it was preserved within the 4 °C refrigerator. It wasdiluted by 0.10 M phosphate buffer solution to obtain the working solutions. Graphene oxide (GO) was provided by JCNANO technology Co., Ltd. Carboxylated multiwall carbon nanotubes (MWCNTs, 95% of purity, length of 0.5-2 μm and diameter of 8-15 nm) were provided by XFNANO technology Co., Ltd. Isoproturon (ISO, 99.00% of purity), the phosphate buffer solution (PBS, 0.10 M) of diverse pH was prepared through blending Na_2HPO_4, NaH_2PO_4, and NaCl (all at 0.10 $mol\cdot L^{-1}$). Meanwhile, PBS of pH 1 was obtained by further adjustment using H_3PO_4 (1.0 $mol\cdot L^{-1}$). The probe solution was prepared by mixing KCl (0.10 $mol\cdot L^{-1}$), $K_4[Fe(CN)_6]$ (5.0 $mmol\cdot L^{-1}$) and $K_3[Fe(CN)_6]$ (5.0 $mmol\cdot L^{-1}$). The remaining reagents were analytically pure, which were utilized as received with no additional purification. The 18.20 MΩ·cml utrapure water was employed for each experiment.

2.2 Apparatus

For each electrode, the elemental composition and surface morphology were characterized by the scanning electron microscope (SEM, SU8220, Hitachi, Japan) as well as the energy dispersive X-ray Spectrometers (EDS, SU8220, Hitachi, Japan). The CHI660E electrochemical workstation was used for electrochemical measurement within the standard three-electrode system under ambient temperature, in which the GCE (diameter, 3 mm) or that after modification was utilized to be working electrode, and the platinum wire served as counter electrode, while the saturated calomel electrode (SCE) was utilized to be the reference electrode.

2.3 Modification of electrode

Before modification, the alumina aqueous slurry (0.05 μm) was used to meticulously polish the GCE for obtaining the mirror-like surface, followed by washing in ultrasonic bath alternating distilled water with alcohol to remove the residual alumina. Before each electrochemical test, the cyclic potential of bare GCE was scanned within the $Fe(CN)_6^{3-/4-}$ probe solution in the range of potential from − 0.2 to +0.6 V, till two redox peaks with clear boundary were detected. To achieve best detection performance, Nafion D521 dispersion was diluted to 0.5% (in weight) with pure water and 0.5% Nafion solution (4 μL) was drop-casted onto GCE, followed by drying with the infrared lamp. Afterwards, that as-prepared electrode was named Nafion/GCE. To compare GCEs, the MWCNTs- and GO-modified GCE were also fabricated[39,40], respectively. To be simply, MWCNTs (1.00 mg) or GO (1.00 mg) was dispersed into the distilled water (1.00 mL), followed by 30 min of sonication. Because the MWCNTs were carboxylated functionalized and GO has high solubility in water, a well homogeneous suspension can be readily obtained via ultrasonication. Then, that prepared suspension (5.0 μL) was coated to the as-polished GCE surface, followed by drying using the infrared lamp. For convenience, MWCNTs- and GO-modified GCE were signed as MWCNTs/GCE and GO/GCE, respectively.

2.4 Electrochemical analysis

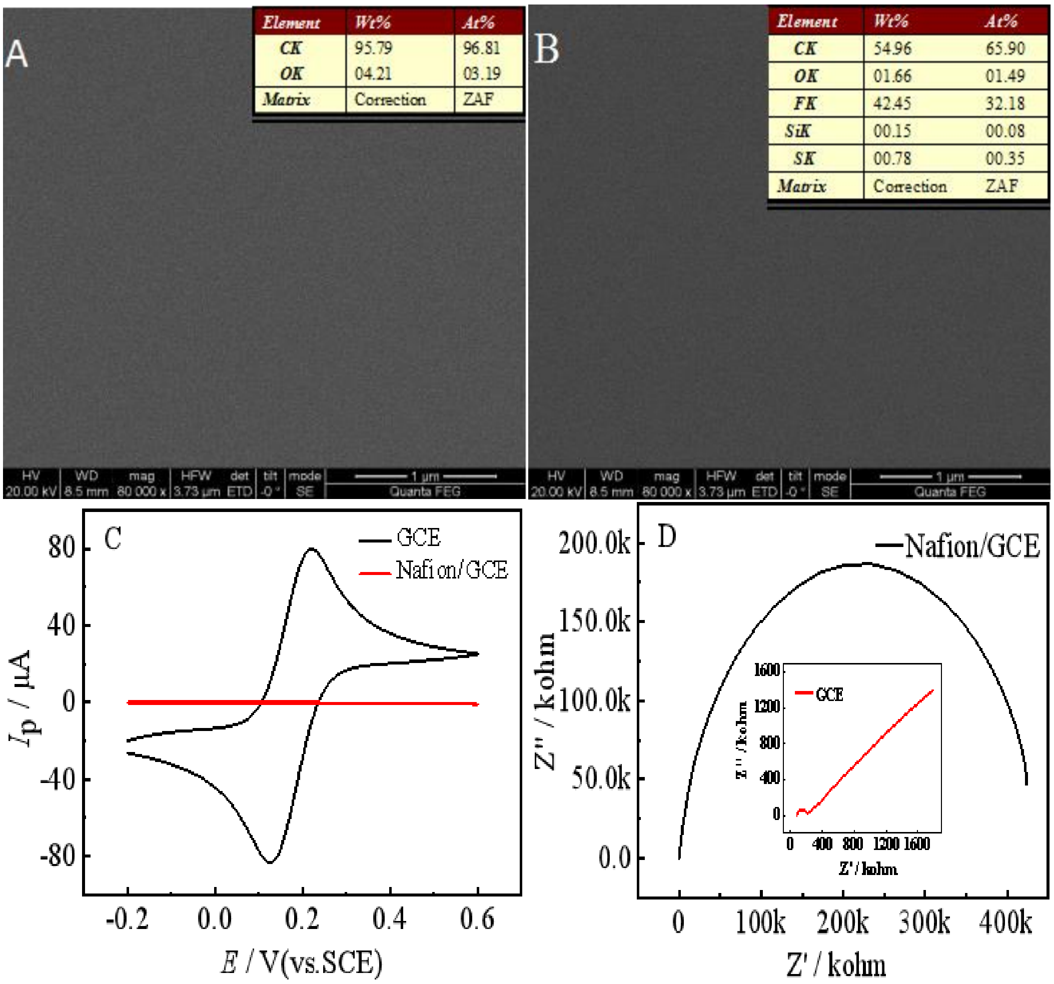
Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterize the electrochemical properties within the $[Fe(CN)_6]^{3-/4-}$ probe solution (5 $mmol\cdot L^{-1}$) supplemented with the KCl supporting electrolyte (0.10 $mol\cdot L^{-1}$). EIS was collected at open circuit potential within the 0.1-105 Hz frequency range and the 5 mV amplitude. CV was collected within the -0.2- 0.6 V potential range and at the 50 $mV\cdot s^{-1}$ scanning rate. CV was conducted to investigate the ISO electrochemical behavior in the solution containing 10.00 $\mu mol\cdot L^{-1}$ ISO at the -0.2 -0.6 V potential range. Square wave voltammetry (SWV) was performed to quantitatively analyze ISO in the specific electrochemical cell supplemented with PBS (5.00 mL, 0.10 $mol\cdot L^{-1}$) within the 0.6 -1.2 V potential range under ambient temperature. ISO concentration within actual samples was detected according to the standard addition approach.

2.5 Preparation of actual test specimens

Lettuce and tomato test specimens were obtained from the local market. The rice field water was collected from the rice paddy field randomly. The tomato and lettuce juices were prepared through crushing appropriate volumes of samples to pulp, followed by removal of residue by filtration. The filtrated juices and paddy water were adjusted to pH 1.0 via the 0.10 mol·L^{-1} PBS prior to test.

3. RESULTS AND DISCUSSION

3.1 Electrochemical characterizations



Element	Wt%	At%
CK	95.79	96.81
OK	04.21	03.19
Matrix	Correction	ZAF

Element	Wt%	At%
CK	54.96	65.90
OK	01.66	01.49
FK	42.45	32.18
SiK	00.15	00.08
SK	00.78	00.35
Matrix	Correction	ZAF

Figure 1. The SEM images and corresponding EDS results of GCE (A) as well as Nafion/GCE (B); CV and EIS (C, D) responses of GCE and Nafion/GCE in $K_3[Fe(CN)_6]$ (5.00 mmol·L^{-1}) and $K_4[Fe(CN)_6]$ (5.0 mmol·L^{-1}) probe solution supplemented with KCl (0.10 mol·L^{-1})

The physical and electrochemical characterizations are displayed in Fig.1. As observed in Fig. 1A and 1B, the surface morphology of Nafion modified GCE, like the polished GCE, is very smooth. Combining with the EDS result, we can conclude that an even layer of Nafion membrane was coated firmly on the surface of GCE. The even distribution of Nafion membrane on the GCE can be attributed to excellent film forming property [41].

Fig. 1C and 1D show the CV and EIS responses of GCE and Nafion/GCE within the $[Fe(CN)_6]^{3-/4-}$ probe solution (5.0 mM), respectively.

As observed from Fig. 1C, two redox peaks with clear boundary were seen on GCE surface, but no signal was collected after Nafion modification, revealing Nafion has no recognition ability or electrocatalytic activity to Fe^{2+}. Furthermore, the resistance of GCE became poor after Nafion modification, showing the Nafion has low electrochemical conductivity.

3.2 Electrochemical Behavior

CV responses of GCE as well as Nafion/GCE to ISO (10.00 μM) in pH = 1.00 are displayed in Fig.2. Only one well-defined cathodic peak centered at 0.99 V was observed for both electrodes, showing the completely irreversible electrochemical oxidation of ISO.

Noteworthily, for Nafion/GCE, its oxidation current was 7.56 μA, which was about 10-fold than that of GCE achieved. Considering Nafion has low electron transfer ability as evidenced by EIS and no obvious response to the $[Fe(CN)_6]^{3-/4-}$ probe solution; therefore, Nafion/GCE's high CV response to ISO is attributed to Nafion specific high catalytic activity to ISO.

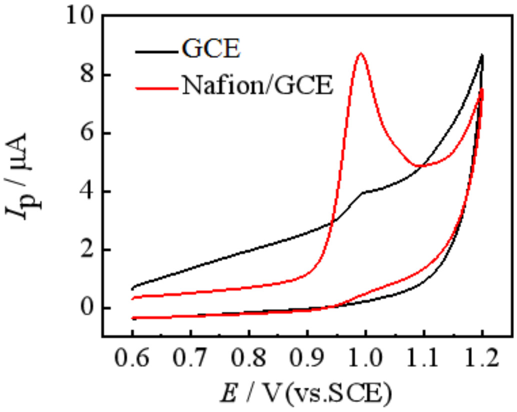


Figure 2. CV responses to isoproturon (10.00 $\mu mol \cdot L^{-1}$) within the 0.10 $mol \cdot L^{-1}$ KCl (pH = 1.0) at the scanning rate of 50 mV S^{-1} (bare GCE and Nafion/GCE)

3.3 Effect of pH

CV responses to ISO at Nafion/GCE within the 0.10 $mol \cdot L^{-1}$ solution with pH ranging from 0.5 to 4.0 are displayed in Fig.3. As expected, the current varied as the change of pH, which suggested that protons participated during the oxidation process. The greatest oxidation peak current occurred at the pH value of 1.0. As a result, pH 1.0 was chosen for following assays to obtain the highest sensitivity.

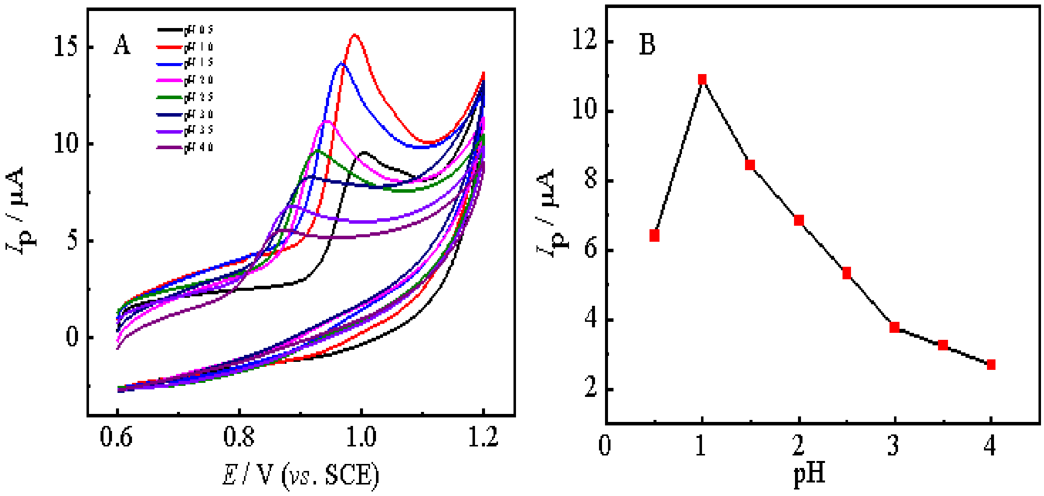


Figure 3. Nafion/GCE CV response to isoproturon (20.00 µmol·L^{-1}) within the 0.1 mol·L^{-1} PBS supplemented with 0.1 mol·L^{-1} KCl at diverse pH

3.4 Effect of scan rate

For obtaining the precise mechanism of action of ISO on Nafion/GCE, the impacts of scanning rate (25~ 400 mV·s^{-1}) on ISO electrooxidation (20.00 µmol L^{-1}) were explored through CV (pH 6.5) (Fig. 4). As presented in Fig. 4A, the potential and peak current gradually increased as the scanning rate increased. Typically, peak current is proportion to the scanning rate square root, which can be expressed as I_p (µA) = 1.9587 (± 0.0341) $v^{1/2}$ (mV·s^{-1})$^{1/2}$ – 1.88836 (± 0.4694) (R^2 = 0.9973), implying a typical electrochemical reaction controlled by diffusion takes place at electrochemical interface. In addition, E_p increases as the rise of scan rate, which obeyed the following regression equation: E_p (V) = 0.0200 (± 0.0006) ln$v$ (mV·s^{-1})+ 0.9142 (± 0.0029) (R^2 = 0.9923). As reported by Laviron [42], the association of E_p with ln$v$ is described below:

$$E_p = E^0 + \frac{RT}{\alpha nF}\ln\frac{RTk^0}{\alpha nF} - \frac{RT}{\alpha nF}\ln v$$

in which E_p stands for the potential of oxidation peak (V), E^0 represents formal potential, R is indicative of universal gas constant (8.314 J·mol^{-1}·K), T stands for temperature (298.15 K), α denotes the coefficient of electron transfer, n suggests the number of electron transfer, F indicates Faraday constant , and v denotes the scanning rate (mV·s^{-1}). Finally, n was determined as 2, so α was 0.6.

Therefore, the proposed reaction mechanism based on a previous report [43], can be presented as Scheme 1. In detail, two molar sulfonic acid groups at the end of the vinylether side chain, combining two molars of electrons, form two molars of hydrogen radical (Step 1). Then, the ISO is catalyzed to phenylamine, CO, and $NH(CH_3)_2$ by the hydrogen radicals (Step 2).

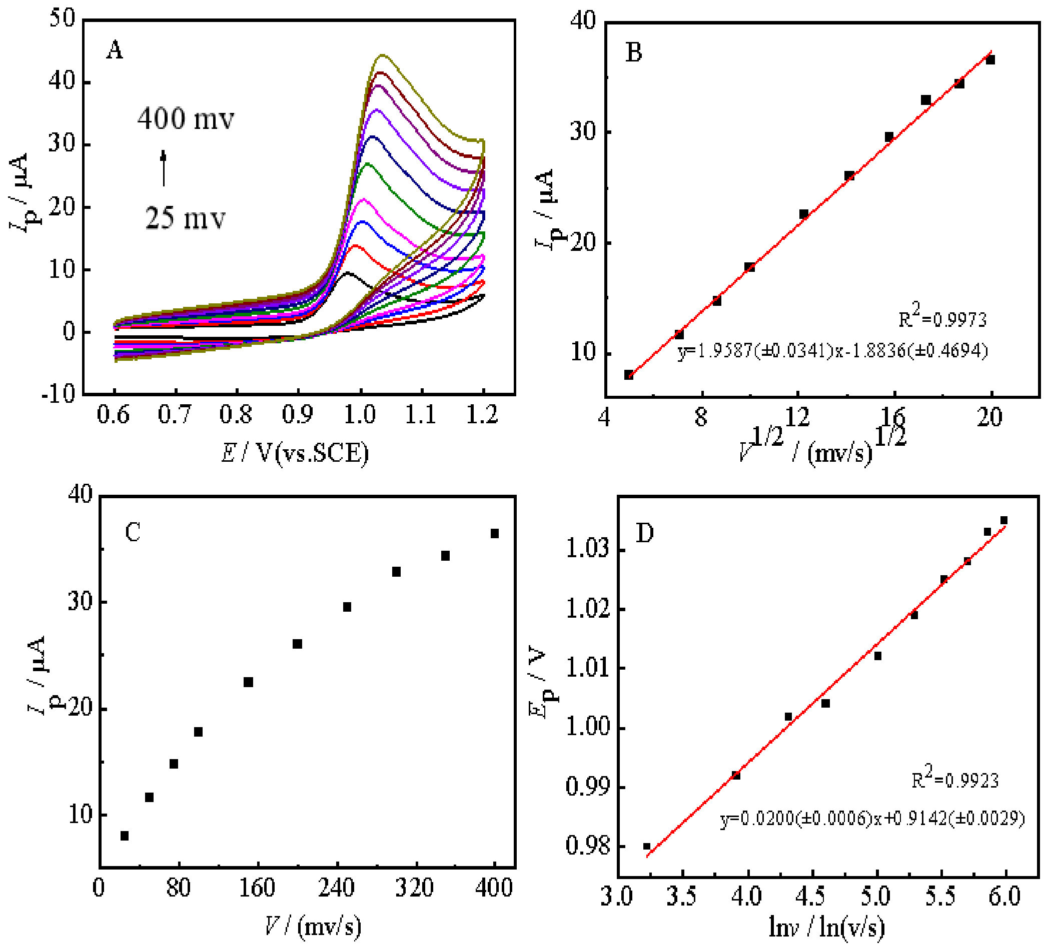
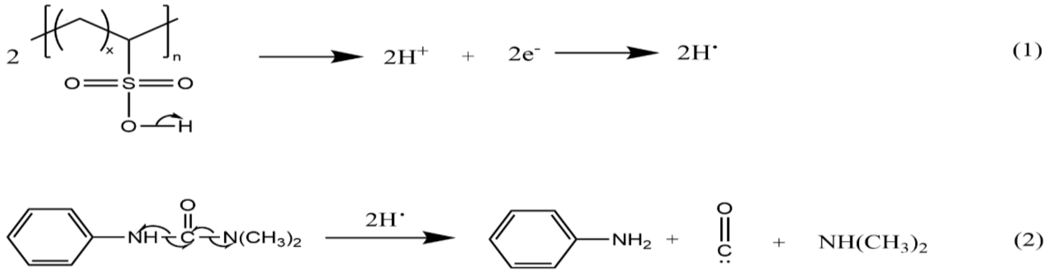


Figure 4. (A) CVs of isproturon (20.00 μmol·L^{-1}) at nafion/GCE in pH =1.0 phosphate buffer solution containing 0.10 mol·L^{-1} KCl at different scan rates (25, 50, 75, 100, 150, 200 ,250, 300, 350, 400 mV·s^{-1}) ; (B) The linear relationship between the oxidation peak current and the square root of the scan rate, (C) The linear relationship between the oxidation peak current and the scan rate, (D) The linear relationship between the oxidation peak potential and the natural logarithm of the scan rate.



Schematic diagram 1. A proposed acid-catalyzed reaction mechanism for ISO over the Nafion modified GCE

3.5 Electrochemical detection of ISO

The SWV method was utilized to investigate the sensor performance in detecting ISO. As shown in Figure 5A, when ISO content increased, its oxidation peak current increased accordingly. Notably, peak current shows a superb linearity to ISO content (range, 0.09 μmol·L^{-1} – 20.00 μmol·L^{-1}) (Figure 5B). The corresponding linear regression equation follows $I_{(ISO)}$ (μA) = (0.5948 ± 0.0073) C (μmol·L^{-1}) - (0.0094 ± 0.0016) (R^2 = 0.9990). The LOD was predicted to be 0.03 μmol·L^{-1} (S/N = 3). The as-determined ISO was compared with previously reported electrochemical sensors. Table 1 lists the results. As far as we know, there are only few senors modified chemically to detect ISO [23, 24, 36], because of the low electrochemical activity ISO and antifouling effect. The sensor developed in this work has the widest linearity range compared to other chemically modified sensors and relative lower LOD. Additionally, this rapid and simple fabrication and detection procedure indicates that the as-prepared sensor may possibly serve as the simple, effective, and cost-effective sensor.

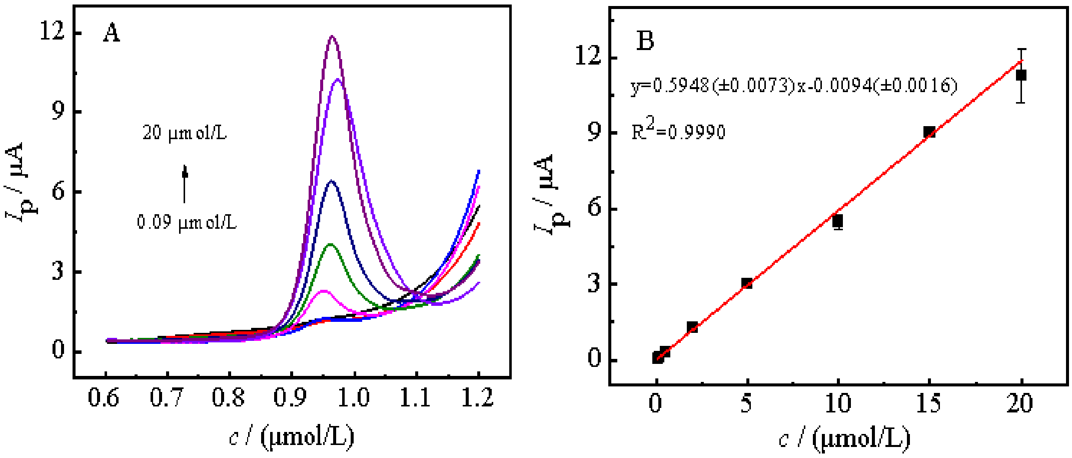


Figure 5. (A) The SWV responses of 0.09, 0.20, 0.50, 2.00, 5.00, 10.00, 15.00, 20.00 μmol·L^{-1} isproturon at Nafion/GCE in 0.10 mol·L^{-1} phosphate buffer solution (pH = 1.0) (B): The linear relationship peak current and concentration.

Table 1. The comparison of different modified electrodes for the determination of ISO.

Modified Electrodes	Method	Liner range (μmol·L^{-1})	LOD (μmol·L^{-1})	Ref
Clay-CMC/GCW	DPSV	0.26 -61.80	-	(Manisankar et al. 2005)
Graphene-SPCE	SWV	0.10 - 48.50	0.10	(Noyrod et al. 2014)
MIP-GCE	SWV	0.009-0.10	0.0028	(Sadriu et al. 2020)
GO-MWCNTs-COOH/GCE	SWV	0.30–15.00	0.10	(Zhou et al. 2020)
Nafion/GCE	SWV	0.09-20.00	0.03	This work

MIP: molecular imprinted polymer; Screen-printed electrode: SPCE.

3.6 Stability, reproducibility, and repeatability

SWV was applied in investigating the Nafion/GCE repeatability through monitoring the peak current for 2.00 µM ISO at one electrode. The results indicate that the Nafion/GCE has strong antifouling effect on the detection of ISO and can be used repeatedly. The relative standard deviation (RSD) for 25 times test is as low as 1.8 %, showing the constructed sensor holds ultra-highly practical application. Considering carbon-based materials were used popularly as the electrode material[46,47], MWCNTs and GO modified GCE were thereby selected as contrast in the detection of ISO, aiming to investigate the antifouling effect. The results reveal that ISO has strong fouling effect on MWCNTs and GO modified GCE (Fig. 6B and 6C), which not the same as the Nafion modified one. The high repeatability of Nafion modified electrode may owing to its inhibition to the transport of reactants and products, as reported in [24].

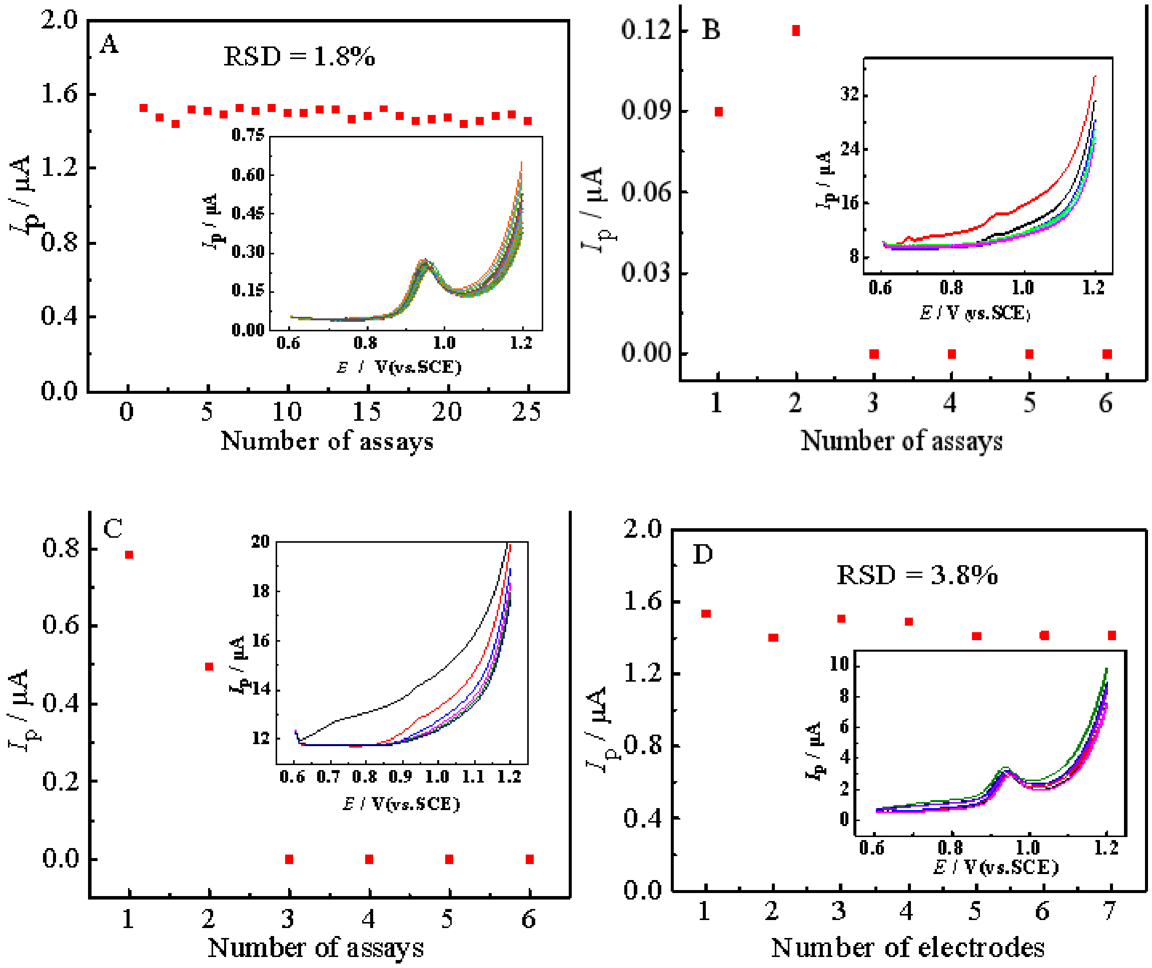


Figure 6. The repeatability measurement of Nafion/GCE (A), MWCNTs/GCE (B) and GO/GCE (C) in 0.10 mol·L^{-1} phosphate buffer solution (pH = 1.0) in 2.00 µmol·L^{-1} ISO by using SWV with one electrode; (D) The reproducibility measurement of Nafion/GCE in 0.10 mol·L^{-1} phosphate buffer solution (pH = 1.0) in 2.00 µmol·L^{-1} ISO by using SWV.

The electrochemical sensor reproducibility was stressed by seven diverse Nafion-modified electrodes at identical content. Our electrochemical sensor shows satisfactory reproducibility with RSD 3.8%, showing the Nafion modified electrode owns high reproducibility (Fig.6 D). Stability represents another important indicator for the electrochemical sensor. The nafion/GCE stability was assessed after preservation at 4 °C for 30 days in the present study. According to our findings, the peak current of ISO was 105% of initial value after 30 days preservation within refrigerator, almost no change compare to its initial stage, indicating high actual application value. In addition, its long-term stability might be because that the catalytic property of Nafion can be regenerated with acid, as reported in this paper[48].

3.7 Interference study

For evaluating the Nafion-modified electrode's selectivity, the interference of potential interferents on the detection of 2.000 μM ISO were investigated. The interferents includes 100-fold of Pb^{2+}, NO_3^- , K^+, Cl^-, vitamin C, one-fold of carbaryl and one-fold of carbendazim. Carvary and carbendazim were analyzed in low fold because they are the typical insecticide and fungicide commonly used in agriculture with almost equal amount to ISO(Fig. 7). The results reveal that these interferents almost has no disturbance (signal change of <5%) during ISO detection, demonstrating the Nafion-based sensor has high selectivity towards the detection for ISO.

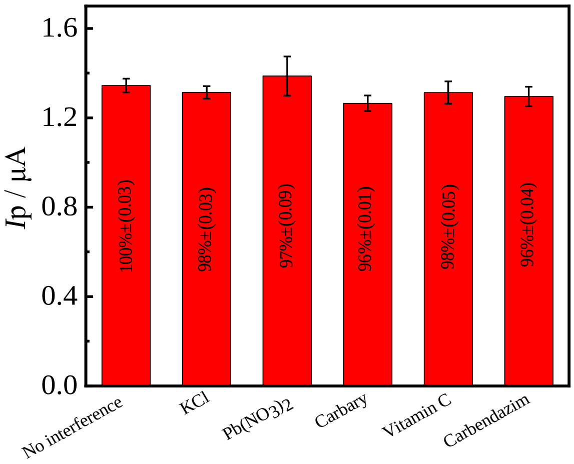


Figure 7. High selectivity of Nafion-based sensor towards the detection for ISO interfered by inorganic ions or organic substances via SWV method at the Nafion/GCE

3.8 Real sample analysis

For assessing our method validity, the lettuce and tomato samples, together with a water sample collected from rice field, were analyzed at optimal conditions using the standard addition method. Each sample were analyzed for 3 times in parallel. According to our findings (Table 2), the recovery rates of the above 3 samples were 92.60%-107.4%, with the values of RSD ranging from 2.1% to 5.6%, showing the electrochemical sensor has admirable creditability and accuracy in detecting ISO within the actual samples.

Table 2. Determination of ISO in various real samples and the spiked recoveries collected by the Nafion modified GCE by using SWV method.

Samples		SWV		
	Spiked $\mu mol \cdot L^{-1}$	Found $\mu mol \cdot L^{-1}$	Recovery %	RSD (n = 3) %
Rice-filed water	0.50	0.47±0.013	94.40	2.7
	5.00	5.29±0.14	105.9	2.6
	20.0	20.33±1.16	101.6	5.6
Tomato	0.50	0.46±0.008	92.70	1.8
	5.00	5.37±0.21	107.4	3.8
	20.00	19.82±0.58	99.10	3.0
Lettuce	0.50	0.49±0.02	97.10	4.5
	5.00	5.17±0.11	103.4	2.1
	20.00	18.51±0.53	92.60	2.8

4. CONCLUSIONS

In this study, a simple electrochemical sensor is developed for the detection of isoproturon via a widely used copolymer Nafion. The sensor is featured by specific recognition, rapid response, and high sensitivity towards ISO detection, owing to the highly catalytical ability to amide in ISO originated from the sulfonic group. Under optimal conditions, our as-prepared sensor exhibits an extensive linearity at 0.09 ~ 20.00 μM, and the LOD value is as low as 0.03 μM, which markedly decreases compared with values stipulated via the European Union legislation. Additionally, our sensor possesses favorable long-term stability, ultra-high repeatability, and superb reproducibility in detecting ISO due to ultral-antifouling ability to ISO, showing highly practical application. Additionally, our sensor is successfully used in ISO determination within the rice-field water, tomato and lettuce with satisfactory recoveries, further evidencing the high reliability and practicability. It is anticipated that the developed sensor will serve as a reliable analytical tool in multiple fields.

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COMPLIANCE WITH ETHICAL STANDARDS

CONFLICT OF INTEREST
Xiaoyi Long, Chaorui Deng , Gansheng Xiao , Fuliang Cheng , Ying Zhou ,
Lei Zhao , Longfei Cai , Jinyin Chen , Juan Du declare that they have no conflict of interest.

NFORMED CONSENT
Not applicable for the nature of this study.

ETHICAL APPROVAL
This article does not contain any studies with human participants or animals performed by any of the authors.

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