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A two component transition metal oxide electrocatalyst for detection ultra-level of an organophosphorus pesticide in real samples

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Abstract

Addressed herein, a two-component transition metal oxide nanocomposite, nickle/cobalt oxide, was synthesized via a hydrothermal method and characterized by X-ray diffraction and scanning electron microscopy. This material was then utilized to modify a pencil graphite electrode. The resulting sensor demonstrated exceptional performance and stability in detecting trace amounts of an organophosphorus pesticide residues present in several real samples. Using the as-prepared martial hybridized with graphene oxide pencil electrode, a broad linear concentration range(40-480nM) and an extremely low detection limit (21nM) were successfully achieved. Also, the fabricated low-cost sensor showed good reproducibility and stability for analysis of chlorpyrifos.

Keywords

Organophosphorus pesticide, Electrocatalyst, Sensor, Pencil electrode

1. INTRODUCTION

Chlorpyrifos (CP), as an organophosphorus pesticide, is extensively employed as an agricultural pesticide, often leaving residual traces in water sources and food products. Its ability to inhibit acetylcholinesterase, an enzyme critical for proper nervous system function, can lead to acute poisoning in humans, causing symptoms ranging from headaches, dizziness, and nausea to seizures and respiratory failure in severe cases [1-3]. Of particular concern is its impact on vulnerable populations: chronic, low-level exposure, especially during prenatal and early childhood stages, has been linked to lasting neurodevelopmental impairments, including autism spectrum disorders [4,5]. Beyond human health, chlorpyrifos presents considerable ecological threats. It is toxic to non-target organisms such as bees, aquatic life, and birds, disrupting local ecosystems and biodiversity [6,7]. Due to its persistence in soil and water, it can leach into groundwater and contaminate food chains, leading to bioaccumulation. These risks have prompted stringent regulations and bans in many countries, yet its continued use in some regions underscores the need for safer agricultural alternatives and ongoing monitoring of residual levels in food and water supplies [8-10].

Conventional analytical methods have been developed to offer high sensitivity and specificity, though they often require sophisticated instrumentation and skilled operation. Methods for detecting ultra-trace levels of chlorpyrifos rely on established analytical techniques that prioritize high sensitivity and definitive confirmation, though they often come with inherent complexities. The gold standard for definitive quantification typically involves chromatographic separation coupled with sophisticated detection. Gas chromatography paired with mass spectrometry (GC-MS) [11, 12] is particularly prevalent, where the sample is vaporized, separated in a column, and the unique mass fragments of chlorpyrifos are identified and

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measured, allowing for detection down to minute ppb range concentrations. high-performance liquid chromatography with mass spectrometric detection (HPLC-MS) serves as a powerful alternative, separating compounds in a liquid phase [13,14]. While these methods provide unparalleled accuracy and are considered reference protocols, they are inherently laboratory-bound, requiring significant sample preparation, costly instrumentation, and highly trained technicians, which limits rapid, on-site application.

Transition metal oxides have emerged as highly promising materials for advancing the electrochemical and optical sensing of pesticides such as chlorpyrifos, offering pathways to simpler, more sensitive, and cost-effective detection platforms[15,16] Their utility stems from a combination of intrinsic catalytic activity, high surface area, tunable electronic properties, and often strong adsorption capacities, which make them particularly suited for interfacing with biological or chemical recognition elements or for acting as direct electrocatalysts. In electrochemical sensors, oxides such as NiO, Co_3O_4, CuO, MnO_2, and their mixed or nanocomposite forms are frequently used to modify electrode surfaces. These materials enhance electron transfer kinetics and can significantly lower the oxidation or reduction overpotential for chlorpyrifos or its enzymatic reaction by products, thereby amplifying the analytical signal [17-19].

As well, transition metal oxides can also facilitate the direct electrochemical oxidation of chlorpyrifos, especially when combined with conductive supports such as graphene oxide or carbon nanotubes. The synergistic effect between the oxide nanoparticles and the conductive matrix enhances both the active surface area and charge transport, enabling the detection of chlorpyrifos at trace levels without the need for complex biological reagents [20,21].

In this study, synthetically produced $(NiCo)O_4$ nanoparticles were employed to modify a pencil graphite electrode. The resulting sensor, designed for simplicity and high sensitivity, was successfully developed to detect chlorpyrifos pesticide residues in vegetable samples, including tomato and eggplant.

2. EXPERIMENTAL

2.1 Materials and methods

The preparation of the $(NiCo)O_4$ nanocomposite followed a standard hydrothermal protocol. Specifically, 0.5 g of $CoCl_2 \cdot 6H_2O$, 1.0 g of $NiCl_2 \cdot 6H_2O$, and 0.9 g of urea were dissolved in 40 mL of deionized water to form a precursor solution. Following 30 minutes of stirring, hydrothermal reaction was carried out at 160°C for 20 hours in a sealed autoclave. The hydrothermally produced powder was isolated, washed exhaustively with water and ethanol, and dried under vacuum (60°C, 6 h). Crystallization was achieved through subsequent calcination in air at 380°C for 3 hours using a heating rate of 5°C per minute. Then, a pencil electrode was loaded by a 1:1 mass portion of $(NiCo)O_4$ and graphene oxide(GO).

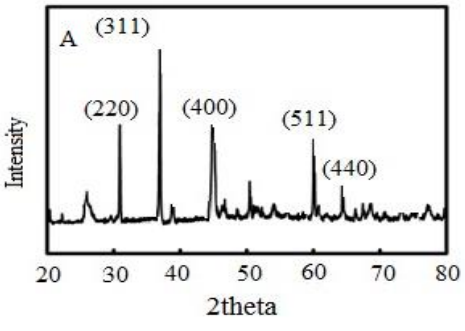
XRD and SEM analyses were conducted to evaluate the crystallinity and morphology of the prepared nanomaterial. A composite was formed by combining it with graphene oxide (GO) to boost its conductive properties and surface area. This $(NiCo)O_4$ /GO composite was subsequently used to modify a pencil electrode, which served as the working electrode in the electrochemical studies.

Electrochemical studies were performed by a galvanostat/potentiostat (Origafelex500, France) equipped with a platin rod as an auxiliary electrode and Ag/AgCl reference electrode.

3. RESULTS AND DISCUSSION

3.1 Characterization of the synthetic nanomaterial

Structural analysis via X-ray diffraction (XRD) validated the formation of the $(NiCo)O_4$ nanocomposite, as its diffraction pattern (fig. 1A) matched perfectly with the JCPDS card No: 20-0781. The pattern displayed distinct peaks at 2θ = 31°, 38.5°, 44.5°, 60°, and 64°, corresponding to the crystallographic planes of the $(NiCo)O_4$, in accordance with published data [22]. Morphological examination using scanning electron microscopy (SEM), presented in fig. 1B, demonstrated that the synthesized material features a distinctive nanostructured morphology resembling cauliflower.



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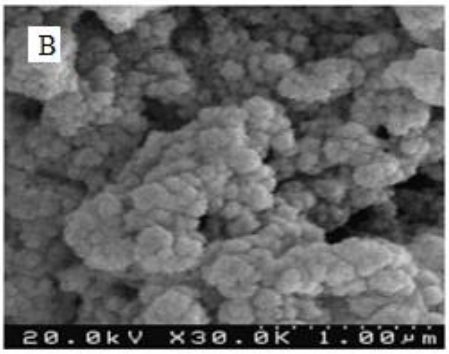

Fig.1, A: XRD pattern, B: SEM image of the $(NiCo)O_4$

3.2. Electrochemical studies

Cyclic voltammetry was employed to characterize the electrochemical performance. The voltammograms in fig. 2A reveal that the bare pencil electrode is electrochemically inactive in the presence of 0.1 mM of chlorpyrifos (CP) in pH= 5 phosphate buffer (PBS) as the optimum pH (curve A). Modification with the $(NiCo)O_4$ /GO nanocomposite introduced a clear redox pair in the blank solution (curve B). Critically, the response of this modified electrode in a 0.5 mM of chlorpyrifos solution (curve C) provided direct evidence of the nanocomposite's synergistic electrocatalytic activity.

Chlorpyrifos contains a phosphorus-sulfur (thionate) bond (P=S). The molecule likely adsorbs onto the electrode surface via interaction between its electron deficient pyridine ring (due to NO_2 and Cl groups) and the metal sites. The two component metal oxide facilitates proton coupled electron transfer and the surface hydroxides (OH) from the metal oxide can act as local proton sources or mediators. For quantitative analysis of chlorpyrifos, differential pulse voltammetry (DPV) was applied for various concentrations of CP (40, 100, 200, 250, 320, 370 and 480nM) dissolved in the buffer solution (pH=5 as the optimum pH). The DPVs were recorded and presented in fig.2B. Following, the corresponded calibration line was plotted (fig.3). As can be seen, an excellent correlation coefficient was obtained among the chlorpyrifos concentrations and peak currents. Herein, the sensitivity was estimated about 0.310µA/nM as the slope of the line.

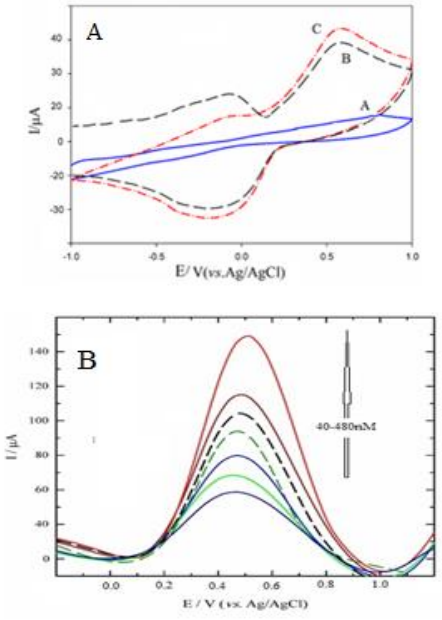

Fig.2, A: cyclic voltammograms of various pencil electrodes, B: DPVs of the $(NiCO)_4$/GO –pencil electrode in different concentrations of CP (range of 40-480nM).

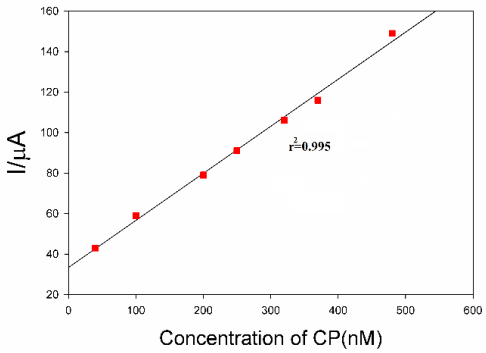

Fig.3, the calibration plot of the related CP concentrations in the range of 40 to 480 nM

The limit of detection (LOD) was calculated via $3S_b/b$. Here, S_b is the standard deviation of 7 times of the blank detection and b stands for the sensitivity. Basically, the LOD was estimated 21nM of chlorpyrifos for the fabricated sensor which confirms the promising performance of the $(NiCo)O_4$ /GO-pencil electrode.

To evaluate the performance of the fabricated sensor in chlorpyrifos pesticide analysis in the vegetable products, a few samples of tomato and eggplant were prepared. An appropriate amount of each vegetable product was placed in a blender and homogenized. The residual liquid in both samples was extracted and stabilized using a phosphate buffer at pH 5. Subsequently, specific quantities of the chlorpyrifos were spiked to the samples and detected by $(NiCo)O_4$ /GO-pencil electrode. The analyte recovery results obtained from the samples

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are presented in table 1. The obtained results confirm the high performance of the fabricated sensor for analysis of the chlorpyrifos in real samples.

Table1. the results of real sample analysis

sample	No	Added CP (nM)	Found CP (nM)	Recovery (%)
tomato	1	100	103.7	103.7
	2	200	198.1	99.05
	3	300	295.5	98.50
eggplant	1	100	96.7	96.7
	2	200	203.0	101.5
	3	300	304.3	101.4

A reproducibility evaluation was conducted on the developed sensor using five independently modified electrodes. These electrodes were employed to measure a 300 nM of chlorpyrifos solution in buffer through DPV method. The calculated relative standard deviation (RSD%) among the measurements was 2.86%, demonstrating satisfactory reproducibility of the sensor.

Additionally, the stability of the $(NiCo)O_4$ /GO-pencil electrode was investigated in two ways. First, a representative modified electrode was stored under ambient conditions for a period of fourteen days. After this duration, it was used to detect a known concentration of chlorpyrifos via DPV. The results showed a reduction in the electrochemical signal (peak current) of less than 5% compared to the initial response, confirming good storage stability.

4.Conclusion

A pencil graphite electrode functionalized with a nickel-cobalt oxide ($(NiCo)O_4$) nanocomposite was employed for the determination of ultra-trace levels of the organophosphorus pesticide chlorpyrifos. The developed sensor exhibited a low detection limit of approximately 21 nM along with high sensitivity in wide range of 40-480nM. Given its effectiveness, low cost and stability, this prepared sensor is proposed as a reliable tool for the sensitive detection of chlorpyrifos residues in vegetable samples.

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یک الکتروکاتالیست دو جزئی از اکسیدهای فلزی واسطه برای تعیین مقادیر بسیار کم یک آفت‌کش ارگانوفسفوره در نمونه‌های حقیقی

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چکیده

در این پژوهش، یک نانوکامپوزیت دو جزئی از اکسیدهای فلز واسطه ، متشکل از اکسید نیکل/کبالت، به روش هیدروترمال سنتز و مورد شناسایی قرار گرفت. این ماده سپس برای اصلاح یک الکترود گرافیتی مغز مداد به کار رفت. حسگر حاصل، عملکرد و پایداری چشمگیری در اندازه گیری مقادیر جزئی باقیمانده یک آفت‌کش اورگانوفسفره در تعدادی نمونه واقعی از خود نشان داد. با استفاده از الکترود مدادی ساخته‌شده از این ماده به صورت ترکیب‌شده با اکسید گرافن، محدوده خطی وسیعی از غلظت و همچنین حد تشخیص بسیار پایینی (۲۱ نانومولار) با موفقیت به دست آمد. همچنین این حسگر الکتروشیمیایی توانست پایداری و تکرار پذیری خوبی از خود نشان دهد. در مجموع با ساخت این حسگر ارزانقیمت می توان به نتایج امیدوار کننده ای برای سنجش آفت کش ارگانوفسفره کلرپریفوس دست یافت.

کلید واژه ها
آفت کش ارگانوفسفوره، الکتروکاتالیست، حسگر، الکترود مغز مداد

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