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In-situ non-covalent dressing of multi-walled carbon nanotubes@titanium dioxides with carboxymethyl chitosan nanocomposite electrochemical sensors for detection of pesticide residues

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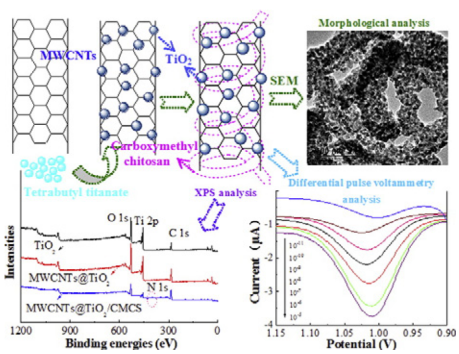
HIGHLIGHTS

- The in situ non-covalent dressing leads to the formation of novel nanocomposites with a synergistic effect.
- The tailor-making of the system composition can tune redox peak currents and reversibility of the modified electrodes.
- The nanocomposite with optimal combination induces significantly strong electrochemical response.
- The fabricated sensors provide an accurate and reliable method for detection of trace pesticides to ensure food safety.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent times, some environmental and health problems are associated with the use of pesticides, which has become a serious concern due to the damage of ecosystem and human health. Hence, it is necessary to design and develop a rapid, prompt and accurate method for determination of trace pesticides. Nanocomposite based electrochemical sensors are a powerful means to execute this task because of their highly-sensitive sensing properties allowing efficient detection of pesticide residues. In the present work, multi-walled carbon nanotubes@titanium dioxides/carboxymethyl chitosan (MWCNTs@TiO_2/CMCS) nanocomposites were prepared by in-situ non-covalent dressing of MWCNTs@TiO_2 with CMCS moieties, while the MWCNTs@TiO_2 was prepared through in-situ sol-gel reaction of tetrabutyl titanate in the presence of MWCNTs. The nanocomposites were characterized by multiple measurement techniques, and the electrochemical properties were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The experimental results indicated that the nanocomposite modified electrodes possessed obvious redox current and reversible electrochemical properties, and could be tuned by altering the composition proportions. The fabricated sensors could be used to efficiently detect pesticide residues, presenting good linear relationship between the trichlorfon concentration and the peak current, a maximal recovery of ca 98.0% and a low detection limit of about 4.0×10^{-7} mol l^{-1}.

1. Introduction

Organophosphorus pesticides (OPs) are a kind of organic compounds that can effectively kill destructive pests or control insects,

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bacteria, weeds, nematodes, rodents, and other pests, and play an important role in enhancing agricultural productivity [1,2]. Although OPs possess low environmental durability and high efficiency, the overuse and misuse will lead to (excessive) residues in food, and enter into the human body through food chains; thus affecting ecosystems and eventually threatening human health [2]. Trichlorfon is one of the widely-used OPs, and the in vivo residues and accumulation in environments and food will cause direct or potential harm to human health. In order to ensure the safety of the food supply and avoid their impact on health, it is significant to construct a rapid, prompt and accurate detection method of trichlorfon residues.

Chromatography is the most widely used analysis method for detection of pesticide residues, which includes gas chromatography and flame photometry (GC-FPD), gas chromatography–mass spectrometry (GC–MS), high performance liquid chromatography-diode array method (HPLC-DAD), and liquid chromatography-mass spectrometry (LC–MS) etc., and has the characteristics of high sensitivity and accuracy [3–5]. However, the traditional method needs expensive equipment, professional operation, complicated sample pre-processing, and time-consuming analysis, thus being unsuitable for on-site detection. Biochemical method is a rapid on-spot qualitative technology for detection of pesticide residues, which includes rapid chemical detection, immunoassay, enzyme-controlling detection and detection in living body etc. [4]. Particularly, the enzyme-controlling method is extensively applied because of its speediness, sensitiveness, simple operation and low cost etc. However, their detection limit and accuracy cannot meet the practical demand. Instrumental analyses, for example Raman spectroscopy, possess very high sensitivity, and can guarantee the precision and veracity of data, but have very tedious process, and very poor reproducibility and stability [3–6]. Electrochemical sensors have attracted extensive attention due to their high sensitivity, simple operation and less expenditure, and they can be applied to the rapid detection of pollutants and pesticide residues etc. [4–8]. In addition, the electrochemical sensors also have the advantages of miniaturization and intelligentization, which offers possibility for on-the-spot detection and analysis. Chemically modified electrodes are very active research area in aspects of current electrochemistry and electroanalytical chemistry, and thus all kinds of modified electrode materials arouse the researchers' interest. Particularly, recent progresses in the area of nanocomposites merit special mention [2,7–14]. As new modified electrode materials, they endow the electrochemical sensors with high sensitivities allowing the efficient detection of pesticide residues.

Nanoscaled TiO_2 is one of the most important semiconductor materials with unique physical and chemical properties, such as small size, large specific surface area and surface activity, good dispersion, absorption and photocatalytic performance, and widely used in preparation of highly-active modified electrodes, solar cell assembly and photocatalytic degradation of organic matter etc. [9,10]. Multi-walled carbon nanotubes (MWCNTs) possess admirable mechanical, electrochemical and optical properties, as well as chemical stability, and have large specific surface area and strong adsorption; therefore, they have received extensive attention in the field of materials science [11]. The combination of carbon nanotubes (CNTs) with TiO_2 will exhibit unique comprehensive advantages, and trigger a synergistic effect. When they are used to modify glassy carbon electrodes (GCEs), the composites are expected to endow the GCEs with more reaction points, to induce strong electrochemical response and significantly to improve the sensitivity [9,10, 12]. However, MWCNTs and nano-TiO_2 are prone to reunite, and thus the dispersion behavior still needs improvements. Carboxymethyl chitosan (CMCS), similar to chitosan (CS), is a kind of water-soluble CS derivatives that have many excellent properties such as good film-forming property, permeability, and adsorbability, etc. Particularly, its good water solubility in comparison with CS makes it easily interact with other materials without pH variation, which improve the dispersion behavior of the systems [13]. Thus, the homogenous system can more easily be formed and wide applications can be found, especially in aspect of electrochemical modified electrodes [13–15]. Up to now, the electrochemical sensors based CS/CNTs composites have extensively been examined [6–8]. To our knowledge, however, the CMCS/CNTs and CNTs/TiO_2/CMCS composite sensors have not been reported yet. Based on the above rationale, it is very meaningful to modify the GCEs with MWCNT@TiO_2/CMCS nanocomposites having excellent dispersion and electrochemical response.

In this work, in-situ sol-gel reaction and solution blending were adopted to prepare new type of MWCNTs@TiO_2/CMCS nanocomposites. This class of the nanocomposites was selected and designed to fabricate electrochemically modified electrodes by mediating the composition ratios of CNTs, TiO_2 and CMCS in the composites. We expect that this combination can trigger strong electrochemical response via the synergistic effect of the three materials, and thus acquire a simple, quick and highly-sensitive electrochemical sensor for detection of pesticide residues in food.

2. Materials and methods

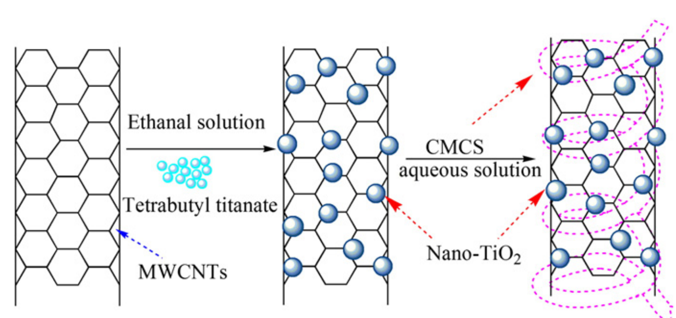
2.1. Materials and reagents

Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, TBT, 99%) was obtained from Beijing J & K Technology Co., Ltd., China. MWCNTs (95 *wt*%, particle diameter 20–30 nm, and length 10–30 μm) were purchased from Chengdu Institute of Organic Chemistry, CAS, and ground to powders in a mortar in advance and then dried in an oven at 120 °C before use. Chitosan (CS, degree of deacetylation 80%, MW 1×10^6) was provided by Shandong Chemical Plant, China. Trichlorfon (Purity 90%) was purchased from Hubei Sharon Once Co., Ltd., China. 5% Nafion ethanol solution (D520) was provided by Dupont Company, USA. Ammonia solution (25%) was purchased from Paini Chemical Reagents Co., Ltd., Zhengzhou, China. Supporting electrolyte solution is a mixture solution containing 0.2 M of PBS and 0.2 M of KCl.

2.2. Preparation procedure

MWCNTs@TiO_2/CMCS nanocomposites were prepared through a two-step strategy, as shown in Scheme 1. Before preparation, CS was modified to obtain CMCS according to the method reported elsewhere [6,14]. For comparison, nanosized TiO_2 was prepared as per a previous report [16,17], as described in 'Supporting information'.

MWCNTs@TiO_2 nanocomposites were prepared through in-situ sol-gel reaction. Simply, MWCNTs with various mass ratios of MWCNTs to TBT were dispersed in absolute ethanol through ultrasonication for 1–2 h. Subsequently, TBT was dissolved in anhydrous ethanol with stirring to form uniform solution. The TBT solution was slowly dripped into the MWCNTs dispersion via constant pressure funnel with constant stirring. Then, acetic acid, 95% ethanol and 0.1 M nitric acid solution were in sequence added to the reaction system, and then aqueous ammonia was



Scheme 1. Schematic diagram of preparation strategy of MWCNTs@TiO_2/CMCS nanocomposites.