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A Co_3O_4 nano-octahedron modified fluorine doped tin oxide electrochemical sensor for detection of benzobicyclon

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ABSTRACT

Unique Co_3O_4 nano-octahedrons for modifying electrode were synthesized through simple chemical reaction. This versatile Co_3O_4 nanostructure possesses the combined advantages of morphological stability and high porosity that can buffer volume change during electrochemical cycles, shorten diffusion path of electron transport, and exhibit remarkable overall electrochemical performance. Samples were characterized by field transmission electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffractometry, Fourier transform infrared spectroscopy and electrochemical impedance spectroscopy. An electrode modified by this material was used for detection of benzobicyclon. Square wave voltammetry showed that there was a linear relationship between peak current and concentration in the range of 10.00–582.96 μmol L^{-1} with a detection limit (S/N = 3) of 0.38 μmol L^{-1}. The modified electrode was used for detection of benzobicyclon in brown rice and rice straw samples with satisfactory recovery, reproducibility and stability. Modified electrodes reported in the literature that were prepared by different methods resulted in other kinds of surface morphologies that did not exhibit the same level of performance.

1. Introduction

Electroanalytical methods have attracted a lot of attention in recent years due to their sensitivity, accuracy, low cost and simplicity [1]. However, in real-world biochemical determination scenarios, they are plagued with interference from small biomolecules that invariably co-exist with the analytes in biological samples. Moreover, individual and simultaneous determination of analytes with conventional electrodes have been very difficult since their oxidation potentials were often severely overlapped and the oxidation products typically fouled the detecting electrodes very quickly [2,3]. Benzobicyclon [BZB, 3-(2-chloro-4-mesylbenzoyl)-2 phenylthiobicyclo[3.2.1]oct-2-en-4-one] exhibits potent herbicidal activity against *Scirpus juncoides*, one of the major troublesome weeds in paddy fields [4]. If people are exposed to it at a level that exceeds the standard, it will cause skin, eye and mucous membrane irritation [5,6]. Ecotoxicological studies reported that BZB in paddy soil was absorbed through the foliage and roots of the plants after paddy water treatment [7]. The maximum residue limit for BZB and its metabolite specified by the central lab of Thai Food and Drug Administration is 0.05 mg/kg. Conventional analytical methods for determination of BZB need lengthy sample pretreatment that costs a lot of time and money and in some cases exhibit low sensitivity and selectivity unsuitable for routine analysis [8]. Thus, development of a working electrode that can discriminate the oxidation potential of BZB from those of interfering substances is vitally important in real-world determination. Development of such electrodes can be achieved by using a modifying material that is electro-catalytically active and gives the desired molecular interaction [9,10].

Nanostructured metal oxides (NMOs) fit the bill as a good modifying material because of their unique optical, surface charge and other electrical properties [11]. NMOs have been extensively investigated for applications such as catalyst, lithium ion battery, supercapacitor, energy storage, gas sensor and electrode materials [12–19]. Various kinds of nanostructure of cobalt oxide (Co_3O_4) have been employed as electrode materials including nanowire [20], nanotubes [21], nanorods [22], nanoflakes [23], nanosheet [24] and nano-octahedrons [25]. Octahedron particles enclosed by (111) facets are advantageously unique due to their excellent catalytic and electrochemical activities as well as environmental friendliness [26–28]. Physical and chemical properties of Co_3O_4 octahedron particles synthesized by reflux method can be suitably controlled and it is simpler to perform than other methods [29–34].

In this work, we synthesized Co_3O_4 nano-octahedrons by a reflux method and developed a procedure for coating them on the surface of fluorine doped tin oxide electrode (FTO). The reasons for using FTO as substrate rather than other substrates that were used for other reported

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modified electrodes were as follows: FTO was used instead of glassy carbon and indium-tin oxide electrodes because FTO does not dissolve in strong acids, bases or organic solvents and FTO is much lower in cost because of the higher natural abundance of fluorine compared to indium [35–37]. The electrochemical behavior of the modified electrode in determination of BZB was investigated by cyclic voltammetry and square wave voltammetry.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent grade. Cobalt chloride ($CoCl_2 \cdot 6H_2O$), ethylene glycol (EG), poly (oxyethyene) 6-nonyl ether (NP6), poly (oxyethyene) 9-nonyl ether (NP9), hydrazine monohydrate, hydrochloric acid (35% HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH), benzobicyclon (BZB) and nafion (~5% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. Potassium dihydrogen phosphate (KH_2PO_4), dipotassium monohydrogen phosphate (K_2HPO_4), phosphoric acid (H_3PO_4) and potassium phosphate tribasic (K_3PO_4) were obtained from Merck. All other reagents and solvents were of analytical grade and double deionized water (DDW) was used throughout the study.

2.2. Synthesis of Co_3O_4 nano-octahedrons

In the synthesis of nano-sized octahedral Co_3O_4, 1.6 g of $CoCl_2 \cdot 6H_2O$ was dissolved in.

150 mL of EG then 20 mL of NP6 was added and stirred for 1 h. After that, the mixture was added with 10 mL of NP9 and stirred intensively for 2 h. Next, the well-stirred mixture was added dropwise with 10 mL of hydrazine monohydrate at room temperature. The mixture was then heated to 120 °C and refluxed for 6 h under continuous stirring. Finally, the product was collected by centrifugation and dried at 80 °C overnight and then dried in the air at 500 °C for 6 h at a heating rate of 5 °C min^{-1}.

2.3. Material characterization

X-ray diffraction (XRD) with a Bruker-Axs D8 XRD, Fourier transform infrared (FTIR) with a Thermo scientific FT-IR Prestige 21 spectrometer, field emission scanning electron microscopy (FESEM) with a Carl Zeiss (AURIGA), transmission electron microscopy (TEM) with FEI Tecnai T20 and energy-dispersive X-ray (EDS) with an INCA Penta FET-3 spectrum were carried out. The Brunauere Emmette Teller (BET) specific surface area was calculated from an N_2 adsorption/desorption isotherm recorded at 77 K with a Quanta Chrome Nova 1000 Gas Sorption Analyzer. The pore size distribution was evaluated by using a Barrette Joynere Halenda (BJH) model.

2.4. Electrochemical performance measurements

Electrochemical study of the modified electrode was performed with AUTOLAB PGSTAT 4.9 potentiostat/galvanostat (ECOCHEMIE, Netherlands) controlled by version 1.10 software. A three-electrode cell system was used consisting of an Ag/AgCl (3.0 M KCl) reference electrode, a platinum wire counter electrode and a working electrode. In a typical procedure, FTO electrodes were polished in 1.0, 0.3 and 0.05 μm alumina slurries, then ultrasonically cleaned in a solution mixture of ethanol:DDW (3:1 v/v) for 15 min and dried in a vacuum oven for 3 h. A working electrode coated with the active material was prepared by first mixing Co_3O_4 nano-octahedron:nafion:DDW in a mass ratio of 8:1:1 into a volume of 10 mL under ultrasonication for 30 min to achieve a paste. The mass of the active material loaded on the FTO in the area of 1 cm × 1 cm was about 5 mg. The coated electrode was dried at 50 °C in a vacuum oven for 5 h then soaked in 2 mol L^{-1} KOH aqueous solution for 24 h to ensure that it was completely saturated with the electrolyte. All measurements including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were performed in 6.0 mol L^{-1} KOH aqueous solution with an electrochemical workstation. EIS test was carried out with a frequency loop from 0.01–10^5 Hz and a perturbation amplitude of 5 mV at an open circuit potential versus Ag/AgCl. The voltage window of CV was from −0.6 to 1.2 V at various scan rates in the range of 5–100 mV s^{-1} and the GCD settings were between 0.0 and 1.2 V with different current densities ranging from 1 to 20 A g^{-1}. The gravimetric specific capacitances of the modified electrode at various scan rates can be calculated on the basis of CV curves according to Eq. (1). From the charge/discharge measurements at different current density, the specific capacitances values of the modified electrodes was calculated based on the galvanostatic charge/discharge curves according to Eq. (2) [38]:

$$C_s = \frac{1}{m\nu(V_a - V_b)} \int_{V_a}^{V_b} I(V)dV \tag{1}$$

$$C_s = \frac{I\Delta t}{m\Delta V} \tag{2}$$

The specific energy density (*E*) and specific power density (*P*) were calculated by Eqs. (3) and (4) [39]:

$$E = \frac{1}{7.2} C_s (\Delta V)^2 \qquad (\text{Wh kg}^{-1}) \tag{3}$$

$$P = \frac{3600 \times E}{\Delta t} \qquad (\text{W kg}^{-1}) \tag{4}$$

where C_s is the specific capacitance (F g^{-1}), *I* is the discharge current (A), *m* is the mass of the electroactive material (g), Δt is the discharge time (s), ν is the sweep rate, $V_a - V_b$ is the potential window (V) and ΔV is the voltage window (V).

Experimental conditions that affected the analysis of BZB such as scan rate (10–550 mV s^{-1}) and pH of phosphate buffer solution (PBS, pH 2.0–12) were also investigated by CV. After the analysis conditions were optimized, square wave voltammetric (SWV) experiments were carried out at the Co_3O_4 nano-octahedron electrode with pulse width = 0.04 s, amplitude = 25 mV, sample period = 0.02 s and pulse period = 0.2 s with the use of a standard addition method. During these experiments, the containing cell was purged with high purity N_2 for 15 min prior to each measurement and kept under N_2 atmosphere during the measurements.

2.5. Preparation of brown rice and rice straws samples

Ten grams of well-ground brown rice samples were passed through a 500 μm sieve screen and placed in a 50 mL Teflon centrifuge tube. Next, 10 mL of distilled water with 10 mL of 2.0 mol L^{-1} NaOH was added to the tube and the mixture was shaken under nitrogen gas at room temperature with a vortex mixer for 15 min. The hydrolysate was acidified to pH 2 with 6.0 mol L^{-1} HCl and centrifuged to separate the cloudy precipitate from the clear supernatant which was then extracted with hexane at a hexane to water phase ratio of 1:1 in order to remove free fatty acids and other lipid contaminants. The liberated phenolic acids were then extracted with ethyl acetate at a solvent to water phase ratio of 1:1. The ethyl acetate extract was evaporated until the sample was dried and then the brown rice compounds were dissolved in 10 mL of methanol and stored at −10 °C prior to further analysis. Before an electrochemical analysis, the samples were diluted to 1:100 with PBS (pH 7.0).

Rice straws were cut into 4–5 cm lengths and thoroughly washed with warm water to remove dirts and aqueous soluble substances, followed by drying at 50 °C. The dried and clean straws were then crushed into powder with a grinder. Rice straw powder was passed through a 420 μm sieve screen. Then, 5 g of it was put in a 250 mL Erlenmeyer