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Simple and novel electrochemical sensor for the determination of tetracycline based on iron/zinc cations–exchanged montmorillonite catalyst



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ABSTRACT

A simple and novel electrochemical sensor for the determination of tetracycline (TC), a kind of antibiotic that may induce residue in the food chain, was developed by the modification of iron/zinc cation–exchanged montmorillonite (Fe/Zn–MMT) catalyst on glassy carbon electrode (GCE). The morphology and the structure of the Fe/Zn–MMT nanomaterial were characterized by scanning electron microscopy and X-ray diffraction, respectively. The results of electrochemical experiments demonstrated that the sensor exhibited excellent electrocatalytic activity to the oxidation of TC in the presence of sodium dodecyl sulfate. The sensor displayed a wide linear range from 0.30 to 52.0 μM and a low detection limit of 0.10 μM by using the derivative differential pulse voltammetry. Moreover, the electrochemical sensor was applied to the detection of TC in feedstuff and meat samples.

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1. Introduction

Antibiotic, used in human and animal medicines for controlling microbial infections, as well as incorporated into livestock and poultry feed to increase feed efficiency and improve the growth rate, induce serious residues in the food chain, which can be responsible for toxic effects, allergic reactions in individuals with hypersensitivity [1], and can result in the emergence of harmful bacteria resistant to antibiotics [2]. Therefore, the presence of residues of antimicrobial agents constitutes a potential risk to the human health, and nowadays these antibiotic residues are also recognized as an emerging environmental problem [3,4]. Owing to the low cost and high antimicrobial activity, tetracycline (TC, Scheme 1) is one of the primarily antibiotics groups used for veterinary purposes, for human therapy and in agriculture sector as feed additive [5,6]. Clinical studies of TC have shown that this group of antibiotics have an auxiliary treatment of tumor, inhibit the activity of collagen enzyme and promote bone absorption [7,8]. However, TC resistance is considered to be the largest resistance against an individual class of antibiotics because this resistance was reported to have over 189 tet genes in bacteria [9]. And tetracycline can be deposited in bones and teeth leading to the inhibition of bone growth [10]. This has spurred

the development technologies for rapid and accurate detection of TC extensively.

Up until now, many analytical methods have been developed for the detection of TC, such as chromatography [11], fluorescence [12], luminescence [13], and electrochemistry techniques [14–22]. Among various approaches, electrochemical sensors for TC have attracted much attention, owing to their advantages of convenience, operation simplicity, and suitability for real-time detection [23,24]. As a result, electrochemical sensors based on DNA [14], aptamer [15], antibody [16] and molecularly imprinted polymer [17] have been fabricated because of their high selectivity and sensitivity. Their application, however, is limited because of their costliness, easy denaturation and complicated immobilization procedure. Thus, the development of a high sensitivity and good selectivity catalyst for direct TC detection is still highly desirable in this field. Calixto et al. [18] evaluated the determination of TC in natural water samples using graphite–polyurethane composite electrode. A detection limit of 2.80 μM was obtained. Masawat et al. [19] fabricated a disposable screen-printed gold electrode to determine TC residues in food with a detection limit of 0.96 μM . A gold modified microelectrode was developed by Wang et al. [20] and used to direct TC detection with a detection limit of 187 nM. The voltammetric behavior of TC at multi-wall carbon nanotube–ionic liquid film modified glassy carbon electrode (GCE) was studied by Guo et al. [21]. The detection limit for TC was estimated to be 30 nM after 150-s accumulation. Otherwise, a low detection limit of 12 nM for the detection of TC based on acetylene black

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electrode in the presence of sodium dodecyl sulfate (SDS) was reported by Dang et al. [22], which showed the sensitizing effect of SDS.

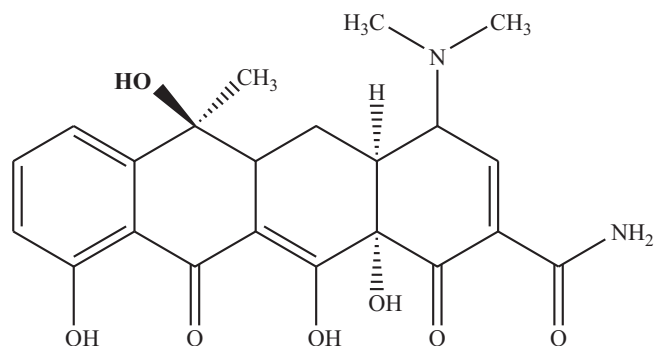
Montmorillonite (MMT) science and its application have received increasingly wide attention in the areas of physics, chemistry, environmental and materials areas because of its abundance, cheapness, environmental compatibility, high surface areas, surface reactivity and cation exchange capacity [25]. The layers of MMT consist of two tetrahedral silica sheets sandwiching one octahedral alumina sheet [26]. And the negative surface charges between the clay platelets are balanced by Ca^{2+} , Mg^{2+} , or Na^+ cations, which can be easily exchanged with other metal cations which could lead to the enhancement of its dispersion in the continuous phase, the increase of surface area, and the exfoliation or intercalation behavior of MMT [27], which in turn improves nanocomposite performance.

In this work, Fe and Zn mixed nanoparticles were intercalated into MMT nanolayers through cations-exchange technique to increase the catalytic ability of MMT considerably. And a simple, rapid and convenient electrochemical sensor for the detection of TC was fabricated using Fe/Zn–MMT as sensing film. The electrochemical behaviors of TC were studied in the presence of SDS. It was found that Fe/Zn–MMT modified GCE greatly increased the oxidation signal of TC, compared with the bare GCE. Fe/Zn–MMT exhibited high accumulation efficiency and remarkably enhanced the surface concentration of TC due to the high surface area and swelling layered structure. As a result, a simple and novel monitoring system was developed for TC. Moreover, the newly developed sensor owns promising application for the determination of TC in real samples.

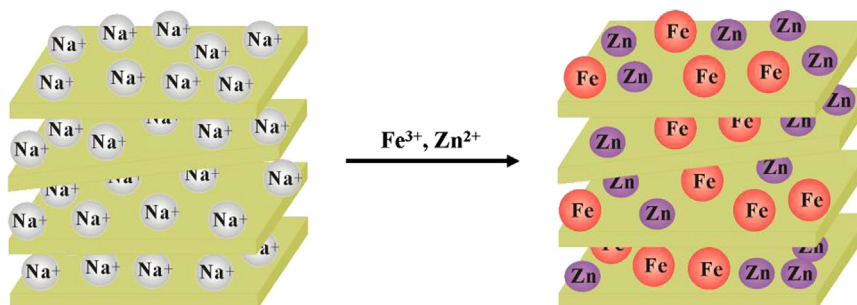
2. Experimental

2.1. Reagents

All chemicals were of analytical grade and used directly. TC (Sigma) was dissolved into 0.1 M HCl to prepare 1.0 mg mL^{-1} standard solution,



Scheme 1. The chemical structure of tetracycline.



Scheme 2. Schematic representation of the cation exchange reaction that leads to Fe/Zn–MMT.

and stored at 4 °C. Anhydrous iron nitrate (FeNO_3), zinc nitrate hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$), SDS, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl benzene sulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Nanosodium MMT ($\sim 25 \text{ nm}$) was obtained from the Fenghong Clay Chemicals Co., Ltd. (Zhejiang, China). The content of MMT was 96–98%, and the apparent density and diameter thickness ratio of the material were $0.25\text{--}0.35 \text{ g cm}^{-3}$ and 200, respectively. Doubly distilled water (the resistivity of which is $1.3 \times 10^6 \Omega \text{ cm}$) was used throughout.

2.2. Apparatus

Electrochemical measurements were performed on a CHI 660E electrochemical workstation. A conventional three-electrode system, consisting of a Fe/Zn–MMT film modified GCE, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed. Scanning electron microscopy (SEM) characterization was conducted with a Hitachi S-4800 microscopy (Japan). X-ray diffraction (XRD) was recorded on a Rigaku D/max-2500, using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) as a source (current intensity, 100 mA; voltage, 40 kV) and a Xcelerator detector.

2.3. Synthesis of Fe and Zn modified MMT

The Fe and Zn modified MMT (Fe/Zn–MMT) was prepared according to Jha et al. [28] with some modification. In a typical preparation, 40 mL of 0.2 M- FeNO_3 and $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ mixed aqueous solution was slowly added into 2.5 g nano-MMT, and stirred for 4 h at room temperature. After filtering, washing with abundant water and being dried in a vacuum oven at 373 K for 2 h, the product was grinded to powder and then calcined in a furnace at 573 K for 3 h with a heating rate of $2 \text{ }^\circ\text{C/min}$, which was denoted as Fe/Zn–MMT. The schematic representation for the preparation of Fe/Zn–MMT was shown in Scheme 2.

2.4. Preparation of the TC sensor

A GCE (diameter of 3 mm) was firstly polished with $0.05 \mu\text{m}$ alumina slurry on silk, and then washed with ethanol/water (1:1, V/V) and water in an ultrasonic bath, each for 1 min. The suspension of Fe/Zn–MMT was prepared by acutely stirring 20.0 mg of Fe/Zn–MMT powder in 10.0 mL water for 24 h. For fabricating the TC sensor, $10.0 \mu\text{L}$ of the obtained Fe/Zn–MMT colloid solution was coated onto the surface of GCE and allowed to dry under an infrared lamp in the air, which was denoted as Fe/Zn–MMT/GCE, too.

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