

Voltammetric determination of 6-thioguanine and folic acid using a carbon paste electrode modified with ZnO-CuO nanoplates and modifier



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ABSTRACT

ZnO-CuO nanoplates and 2-chlorobenzoyl ferrocene, were synthesized and used to construct a modified carbon paste electrode. The electrooxidation of 6-thioguanine at the surface of the modified electrode was studied. Under the optimized conditions, the square wave voltammetric (SWV) peak current of 6-thioguanine increased linearly in the concentration range 0.05 to 200.0 μM and detection limit of 25 ± 2 nM was obtained for 6-thioguanine. The prepared modified electrode exhibits a very good resolution between the voltammetric peaks of 6-thioguanine and folic acid which makes it suitable for the detection of 6-thioguanine in the presence of folic acid in real samples.

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1. Introduction

The thiopurine drugs, such as 6-thioguanine are used to influence immune response in the treatment of inflammatory diseases such as ulcerative colitis, dermatitis and rheumatoid arthritis, and to stop rejection of tissues posttransplant. Also 6-thioguanine is one of the most important anticancer therapeutic agents used in the clinical treatment of acute childhood lymphoblastic leukemia, inflammatory bowel disease, Crohn's disease, AIDS, and some other pathology [1,2].

Some methods for the determination of 6-thioguanine have been reported such as high-performance liquid chromatography [3] and fluorimetric [4] methods. However, in almost all the methods mentioned above some laborious sample treatment, specific detector, expensive apparatus and complex derivation steps are needed. Also the sensitivity of these procedures falls far short of requirements. Obviously, because of its low operating costs, simple equipment, as well as the widespread use of common laboratory, electrochemistry has been the important analytical method to the chemical workers of analysis [5–8].

Folic acid or folate is a B vitamin. It is also referred to as vitamin M, vitamin B₉, pteroyl-L-glutamic acid, and pteroyl-L-glutamate [9]. Folic acid is a well-known water-soluble part of vitamin B-complex which found in vegetables, fresh fruit, yolk and liver. It is essential for the growing and differentiation of cells. What is more, folic acid is a routine

medicine for pregnant women and a treatment for preventing megaloblastic anemia [10]. Folic acid deficiency may cause mental devolution, neural tube defects, congenital anomalies of spine and brain, foetal development defects and heart attack.

Therefore, various methods for the determination of folic acid such as fluorimetry, spectrophotometry, high-performance liquid chromatography, capillary zone electrophoresis, and flow injection analysis are used. However, the above mentioned methods have some disadvantages such as being time-consuming, laborious, tedious and requiring expensive, narrow range of determination, require heating or extraction and large facilities. On the other hand, because of electroactivity of folic acid, electrochemical techniques have been developed for determination of folic acid with the advantages including high sensitivity, high accuracy less expensive instruments, more convenient procedure and good selectivity [11–17].

Using chemically modified electrodes (CMEs) have some benefits such as decrease of the potential required for the electrochemical reaction to occur and enhancement of the sensitivity due to catalytic activity. Choosing the most convenient modifier for each analyte is very important in CMEs utilization in speciation work, due to affect of modifier characteristics on the sensitivity and selectivity of the electroanalytical response [18–25].

Carbon-paste electrodes (CPEs) are widely used for the electrochemical determinations of a various biological and pharmaceutical species due to their low residual current and noise, ease of fabrication, wide anodic and cathodic potential ranges, rapid surface renewal, and

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low cost. Moreover, chemically modified electrodes (CMEs) can be easily prepared by adding different substances to the bulk of CPEs in order to increase sensitivity, selectivity, and rapidity of determinations [26–34].

In the past few decades, nanoparticles of a variety of shapes, sizes and compositions exhibit excellent conductivity and fascinating catalytic properties, which make them suitable for constructing novel electrochemical sensors for simultaneous determination. Nanocomposites can significantly improve the electrocatalytic properties of substrates, decrease the overpotential, increase the reaction rate and improve reproducibility of the electrode response in the area of electroanalysis. The results indicate that nanocomposites modified electrodes show an enhanced response for the determination of various important biological and clinical species [35–43].

To the best of our knowledge, no study has been published so far reporting the simultaneous electrocatalytic oxidation determination of 6-thioguanine and folic acid by using 2-chlorobenzoylferrocene/ZnO-CuO nanoplates modified carbon paste electrode (2CBFZCCPE). Thus, in the present work, we describe the preparation of 2CBFZCCPE and investigate its performance for the electrocatalytic determination of 6-thioguanine in aqueous solutions. We also evaluate the analytical performance of the modified electrode for quantification of 6-thioguanine in the presence of folic acid. Finally, in order to demonstrate the catalytic ability of the modified electrode in the electrooxidation of 6-thioguanine and folic acid in real samples, we examined this method for the voltammetric determination of 6-thioguanine and folic acid in some pharmaceutical and biological samples.

2. Experimental

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302 N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the 2CBFZCCPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. 6-thioguanine, folic acid and all other reagents were of analytical grade from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–12.0.

2.2. Synthesis of ZnO-CuO nanoplates

Formation of composite of ZnO-CuO nanoplates were started by preparation of solution included CuCl_2 (0.001 M) and ZnCl_2 (0.05 M) at pH = 11.7. The solution was kept at 70 °C for 2 h. The pH of solution was adjusted by ammonia solution (25%). Synthesis process was completed by increasing of temperature to 95 °C for 3 h. After preparation and precipitation of ZnO-CuO nano plates, the precipitate was centrifuged at 15,000 rpm for 20 min. Separated precipitate was washed by methanol and water three times, respectively. Finally, it was dried in 70 °C for 2 h. Typical SEM of ZnO-CuO nanoplates is shown in Fig. 1.

2.3. Synthesis of 2-chlorobenzoyl ferrocene

To a 100 ml round-bottomed flask under argon atmosphere, 1.86 g (10 mmol) of ferrocene, 1.75 g (10 mmol) of 2-chlorobenzoyl chloride and 20 ml of dichloromethane is added. The reaction mixture is cooled in an ice bath (0–5 °C), then 1.40 g (11 mmol) of anhydrous aluminum chloride added in small portions at such a rate that the reaction mixture remains below 5 °C. The resulting solution is stirred for 30 min at 0–5 °C and 2 h at room temperature. Then, the flask is placed in ice bath again

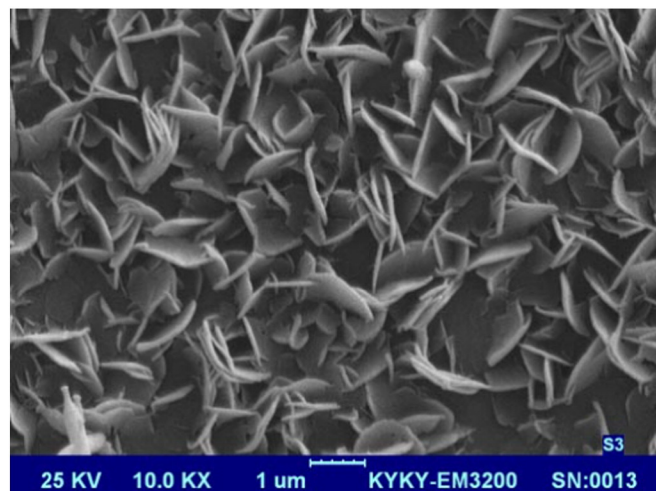


Fig. 1. SEM image of ZnO-CuO nanoplates.

and 20 ml of water is added cautiously to give a two-phase mixture. After stirring for 30 min the aqueous layer is extracted with two 15 ml portions of dichloromethane. The combined dichloromethane extracts are washed once with water, twice with 10% sodium hydroxide solution, dried over magnesium sulfide and evaporated at reduced pressure. The crude residue is purified by recrystallization from heptane to afford (2-chlorobenzoyl)ferrocene in 95% yield. M.p. 99–100 °C,

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 4.30 (s, 5H), 4.62 (t, $J = 1.6$ Hz, 2H), 4.77 (t, $J = 1.6$ Hz, 2H), 7.36 (dt, $J = 1.6, 7.6$ Hz, 1H), 7.42 (dt, $J = 2.0, 7.6$ Hz, 1H), 7.47 (dd, $J = 1.2, 8.0$ Hz, 1H), 7.52 (1.6, 7.2 Hz, 1H).

IR (KBr) (ν_{max} , cm^{-1}): 3080.8, 3052.5 (C–H Aromatic), 1644.9 (C=O), 1442.7, 1292.8, 1031.5, 827.7.

2.4. Preparation of the electrode

The 2CBFZCCPEs were prepared by hand mixing 0.01 g of 2CBF with 0.95 g graphite powder and 0.04 g ZnO-CuO nanoplates with a mortar

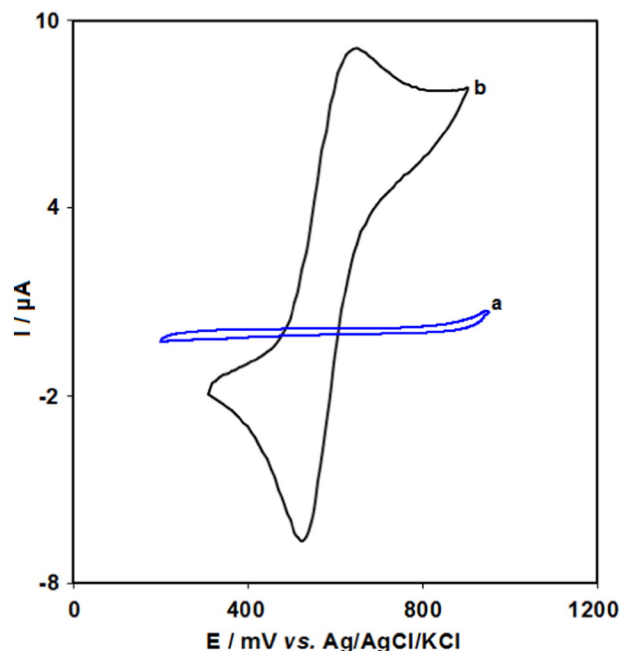


Fig. 2. CVs of CPE (a) and 2CBFZCCPE (b) in 0.1 M PBS (pH 7.0) In all cases scan rate is 100 mV s^{-1} .

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