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NiO nanoparticles modified carbon paste electrode as a novel sulfasalazine sensor

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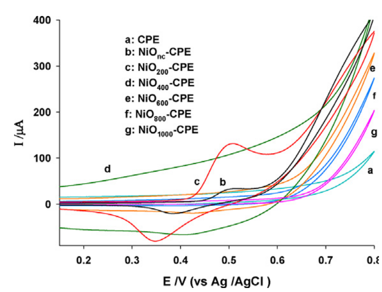
HIGHLIGHTS

- Good activity of NiO-CPE for indirect voltammetric determination of SSZ.
- Needing strong basic pH > 13 for electro-oxidation of NiO to NiOOH.
- Significant dependence of calcinations temperature of NiO on the peak current of NiO-CPE electrode.
- Increase in oxidation peak current of NiO electro-oxidation in the presence of SSZ.

GRAPHICAL ABSTRACT



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ABSTRACT

The sol-gel synthesized NiO nanoparticles were characterized and used for the modification of a carbon paste electrode (CPE) in electrocatalytic voltammetric determination of sulfasalazine. Calcination temperature of NiO had an important role on the peak current of the modified NiO-CPE and calcined NiO at 200 °C had the best and maximum peak current for the corresponding electrode. Jahn-Teller and a Z-out effects for the singlet electrons in their $3d_z^2$ orbital for calcined NiO at 200 °C relatively instable such electrons and hence they can easily participate in the electro-oxidation process. The electrochemical impedance spectroscopy (EIS) results confirmed that the modified CPE by calcined NiO at 200 °C has lower charge transfer resistance. In interaction effects study between the experimental variables by using the response surface methodology (RSM) approach, the optimized run included the 17.5% of NiO modifier, 0.5 M NaOH, amplitude of 295 mV, step potential of 7 mV and frequency of 15 Hz. A calibration plot in the range of 0.009–1.6 μM with limits of detection (LOD) and quantification (LOQ) of 0.002 and 0.006 μM was obtained, respectively. The modified electrode showed good selectivity and applicability for SSZ determination in complex matrixes.

1. Introduction

An autoimmune disease is Rheumatoid arthritis (RA) which causes disordered and systemic inflammation of the synovial joints. This in turn affects other tissues and organs such as the lungs, pericardium and sclera. The painful and disabling effects of RA decrease the personal mobility and functioning and finally limit the

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economic activities. Sulfasalazine (SSZ: 5-[4-(2-pyridylsulfamoyl) phenylazo] salicylic acid) belongs to the anti-inflammatory class of azo-salicylic acid derivatives and can be used as a drug for the treatment of RA and the other types of inflammatory arthritis, such as psoriatic arthritis, and for the treatment of ulcerative colitis and Crohns disease. Due to low solubility of SSZ, it can be absorbed still poorly into the blood stream at pH 8.0–9.0 (due to its higher solubility in alkaline media). However, low solubility and absorption cause to reduced biodisponibility of the drug (around 15%). Hence, an increased SSZ daily dose (about 2–3 g per day) is necessary [1,2]. In clinical practice, SSZ is employed as 5-aminosalicylic acid (5-ASA) precursor. The active part, 5-ASA, can be produced in the colon via reduction of azo-bridge by bacteria. 5-ASA can block the activity of cyclooxygenase and lipoxygenase thereby reducing the production of prostaglandins, resulting to reduced inflammation. However, SSZ is well known drug for disease-modifying anti-rheumatic that decreases the symptoms and slow-down the progress of rheumatoid arthritis, psoriatic arthritis, ankylosing spondylitis, and juvenile rheumatoid arthritis. In other point of view, the structure of the sulfonamide antibiotics is similar to *p*-aminobenzoic acid (*p*-ABA) and interferes with nucleic acids synthesis in sensitive microorganisms. This can take place by blocking the *p*-ABA conversion to the dihydrofolic acid coenzyme (as the reduced form of folic acid) [3–5]. Hence, monitoring and quantitative determination of SSZ has interested for analytical chemists.

So far, different analytical techniques have been used for the detection and quantification of SSZ in the presence of other sulfonamides [6,7]. In general, electrochemical reduction of azo-salicylic compounds at the azo nitrogen atom (in SSZ and some chemical structure similar to SSZ) cleavages the azo bond and releases the 5-ASA [1,8,9]. In other word, the aromatic ring of such compounds undergoes an oxidation process followed nucleophilic addition of water, resulting to production of benzoquinone derivatives correspond to the degree and position of substituents in these rings [10,11]. In other alternative, the electrochemical behavior of pharmacological compounds gives useful informations for study of their mechanism of action [1]. Hence, some works have been reported for the electroanalytical study of SSZ by different modified electrodes [1,8,9]. In general, modified electrodes have been widely used in different analytical determinations due to their enhanced selectivity and sensitivity [12–26].

The metal oxide nanoparticles (NPs) have been widely used in recent years in different research fields, because their particle/crystallite size, morphology and crystalline phase can control their physicochemical properties [27–30]. Nickel oxide NPs as p type semiconductor with wide band gap in the range of 3.6 eV–4.0 eV have been found different physico-chemical applications in catalysis, solar and fuel cells, adsorbents, magnetic and antibacterial materials, gas and electrochemical sensors [31–36].

In this work, NiO NPs were synthesized via a cheap and easy method and applied in the modification of carbon paste electrode (CPE). The resulted NiO NPs-CPE electrode was then used for the voltammetric determination of SSZ. Comparison of this modified electrode with other used for SSZ determination [8–10,23] and other modified electrodes by NiO confirms that construction of this electrode is very easy and no need to other intermediates. In the most published papers on the modified electrodes by metal oxides, pure metal oxide reagents have used for the modification process, but in the present work, effect of calcination temperature of calcined NiO NPs on the behavior of the modified carbon past electrode was studied. This study was done because calcination temperature affects the crystallite phase of NiO and hence its electrochemical properties, and as shown in next sections good results were obtained. In addition, to study the interaction effects between the experimental variables on the electrode response, the experiments were designed by using response surface methodology (RSM) approach [37–40].

2. Experimental

2.1. Reagents and preparations

Graphite powder, sulfasalazine (SSZ), nickel(II) acetate tetra hydrate, citric acid, Nujol oil and other used chemicals with analytical grade purity were purchased from Merck or Aldrich. SSZ tablet (500 mg) as real sample from Mehr Pharmacy Company (Tehran, Iran) was purchased from local drug stores. Triply distilled-deionized water was used for preparation of the solutions. A 0.5 μM stock SSZ solution was prepared daily and used for preparation of more dilute solutions via serial dilution method. Supporting electrolyte was 1 M NaOH solution.

For preparation of SSZ real sample, one pulverized tablet was weighed accurately. An adequate amount of the resulted powder was dissolved in 1 M NaOH solution in a 25 mL volumetric flask and sonicated for 5 min [5]. The serum sample was prepared from Shafa laboratory (Shahrekord, Iran) and stored in a refrigerator after collection. A 600 μL of the serum sample was spiked with 600 μL of SSZ solutions with different concentrations followed by addition of 500 μL acetonitrile to deproteinize the serum. The resulted solution was centrifuged at 12000 rpm for removing the precipitated proteins. The clear supernatant was dissolved in 1 M NaOH solution in a 25 mL volumetric flask [5].

For the sol-gel synthesis of NiO NPs, 2.5 g nickel(II) acetate tetra hydrate was dissolved in 50 mL water and added dropwise into a beaker containing 1.92 g citric acid as ligand. Then nitric acid was added to adjust pH at 3–3.5. The resulted clear solution was magnetically stirred at 65 °C until a highly viscous residual was obtained. After air drying, a gel precursor was resulted. Finally, the resulted light green product was calcined at different temperatures for 6 h [41,42].

Typical procedure for preparation of carbon paste (containing about 10% w Nujol oil) and carbon paste electrode by using insulin syringe has reported in the previous work [43]. For this goal, graphite powder- Nujol oil mixture was thoroughly hand mixed in an agate mortar for 20 min to obtain a homogeneous carbon paste (CP). To modify the resulted carbon paste, adequate amounts of NiO NPs modifier were added to resulted CP (correspond to 5–20 w% of the modifier) and thoroughly hand mixed again for 20 min to obtain a homogeneous modified carbon paste (NiO NPs-CP). For construction of the modified electrode (NiO NPs-CPE), the resulted modified paste was added into the end of an insulin syringe and pressed thoroughly by mechanical force. Then, a copper wire was forced at the end of the syringe to achieve the electrical contact. Similar procedure was used for construction of the raw carbon paste electrode (CPE) using the raw CP. The electrodes kept in open air when not in use. When the electrode response tended to diminish, the surface of the electrode was polished on a soft paper and then rinsed with ethanol and water, respectively.

2.2. Apparatus and voltammetric procedure

XRD pattern of the as-synthesized NiO NPs was recorded by a XRD diffractometer (X'PertPro, with Ni-filtered NiKa radiation at 1.5406 Å, V: 40 kV, i: 30 mA; Netherland). Electrochemical impedance spectra (EIS) were recorded by a Ivium (IEC 61326, Netherland). A PerkinElmer Spectrum 65 FT-IR spectrophotometer (using KBr pellet), Field Emission Scanning Electron Microscopy (FESEM) Mira 3-XMU were used for characterization of the raw and modified samples A Jenway pH meter (model 3505) was used for adjustment of solution pH.

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