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Voltammetric amplified sensor employing RuO_2 nano-road and room temperature ionic liquid for amaranth analysis in food samples

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The voltammetric performance of carbon paste electrode modified with RuO_2 nano-road (RuO_2/NR) and 1,3-dipropylimidazolium bromide (DPIBr) (CPE/RuO_2/NR/DPIBr) was investigated for the determination of amaranth. RuO_2/NR synthesized by sol gel method and characterized by X-ray powder diffraction (XRD), MAP analysis, scanning electron microscopy (SEM) and elemental analysis (EDAX) methods. The result revealed that electrochemical oxidation of amaranth is relative to pH value (one electron and one proton) with an irreversible oxidation signal. The linear response range of 0.008–550 μM and detection limit of 3.0 nM were found to determination of amaranth using CPE/RuO_2/NR/DPIBr at pH = 7.0. CPE/RuO_2/NR/DPIBr showed good ability for determination of amaranth in food samples.

1. Introduction

Electrochemical methods are powerful tools in biological and chemical research works [1–7]. Due to fast response and simple operation, electrochemical sensors are useful selection for food compounds analysis [8–13]. Currently, voltammetric methods have almost been completely suggested in food quality control laboratories [14–17]. Fast and simple preparation of analytes with highly sensitivity is the main advantage of voltammetric methods for food samples analysis [18,19]. In the recent years, modified electrodes improved the abilities of voltammetric sensors for nanomolar and picomolar analysis of biological and food compounds [20–23]. Modification of working electrodes with conductive materials such as polymers, molecularly imprinted, nanomaterials, and ionic liquids help to increasing of sensitivity and selectivity electrochemical sensors [24–34]. According to the above points, electrochemical methods suggested for food analysis as an alternative to chromatography methods.

Ionic liquids have many unique properties, such as high electrical conductivity, non-flammability and chemical stability [35–39]. Due to wide electrochemical windows and good electrical conductivity, ionic liquids were suggested for modification of electrochemical sensors in voltammetric analysis [40–43].

Nanomaterials were considered for modification of electrochemical sensors due to high surface area and low charge transfer resistance [44–46]. Some published papers reported coupling of ionic liquids and nanomaterials for fabrication of high sensitive voltammetric sensors in the recent years [47–49].

In the presence work, we synthesized RuO_2 nano-road by sol-gel method and application of it for modification of carbon paste electrode in the presence of 1,3-dipropylimidazolium bromide as a conductive binder. CPE/RuO_2/NR/DPIBr shows high performance ability for quantification of amaranth in nanomolar level. In continuous, CPE/RuO_2/NR/DPIBr was used as a high performance electrochemical sensor for voltammetric determination of amaranth in food samples.

2. Experimental

2.1. Materials and apparatus

Electrochemical experiments were performed using an Autolab system. A conventional three-electrode system was used with CPE/RuO_2/NR/DPIBr (geometric area 0.284 cm^2), Ag/AgCl/KCl_{sat} and Pt wire as the working, auxiliary and reference electrodes, respectively. Amaranth, starch, ruthenium chloride, ammonia and phosphoric acid

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were purchased from Sigma-Aldrich. KYKY-EM3200 digital scanning electron microscope was used for morphological investigation of RuO_2/NPs. The X'Pert Pro MPD (PANalytical) was used for XRD investigation.

2.2. Synthesis procedure for RuO_2/NR

Firstly, 0.8 g of starch and 80 ml of water mixed together and placed in a 60 °C water bath to achieve a clear solution. 0.012 mol ruthenium chloride salt was added to the clear solution, and then set pH to 10.0 with 1.0 M ammonia. The color of solution changed to black. The solution were stirred for 2 h and then filtered. After washing with water and ensuring complete withdrawal of chlorine, precipitated was dried and calcined at 450 °C for 2 h.

2.3. Preparation of CPE/RuO_2/NR/DPIBr

CPE/RuO_2/NR/DPIBr was fabricated by mixing of 100 mg of RuO_2/NR, 900 mg of graphite powder and suitable amount liquid paraffin (80% w/w) and DPIBr (20% w/w) as binders. The above mixture was mixed for 3 h for obtaining a good paste. The obtained paste was added to the end of glass tube and a copper wire insert in paste for electrical connection devices.

2.4. Real sample preparation

Orange, orangeade and apple juices were purchased from a Kerman, Iran and used directly without any pretreatment.

3. Result and discussion

3.1. RuO_2/NR characterization

SEM image of RuO_2 nano-road is shown in Fig. 1A. The obtained result show that the most of the particles are in rods shape. The MAP and EDAX analysis of RuO_2 nano-road are presence in Fig. 1 B&C. As can be seen, Ru and O elements are presence in synthesized nano-powder that confirms high purity of RuO_2 nano-road.

X-ray diffraction pattern of RuO_2 nano-road synthesized in this work are shown in Fig. 2. The presence of miller indexes of (110); (101); (200); (211); (220); (002); (310); (112); (301) and (202) in 2θ range of 28.2137; 35.1206; 39.7071; 54.3658; 58.1207; 59.3685; 65.3274; 66.7619; 69.1320 and 73.7794 confirm tetragonal structure for RuO_2

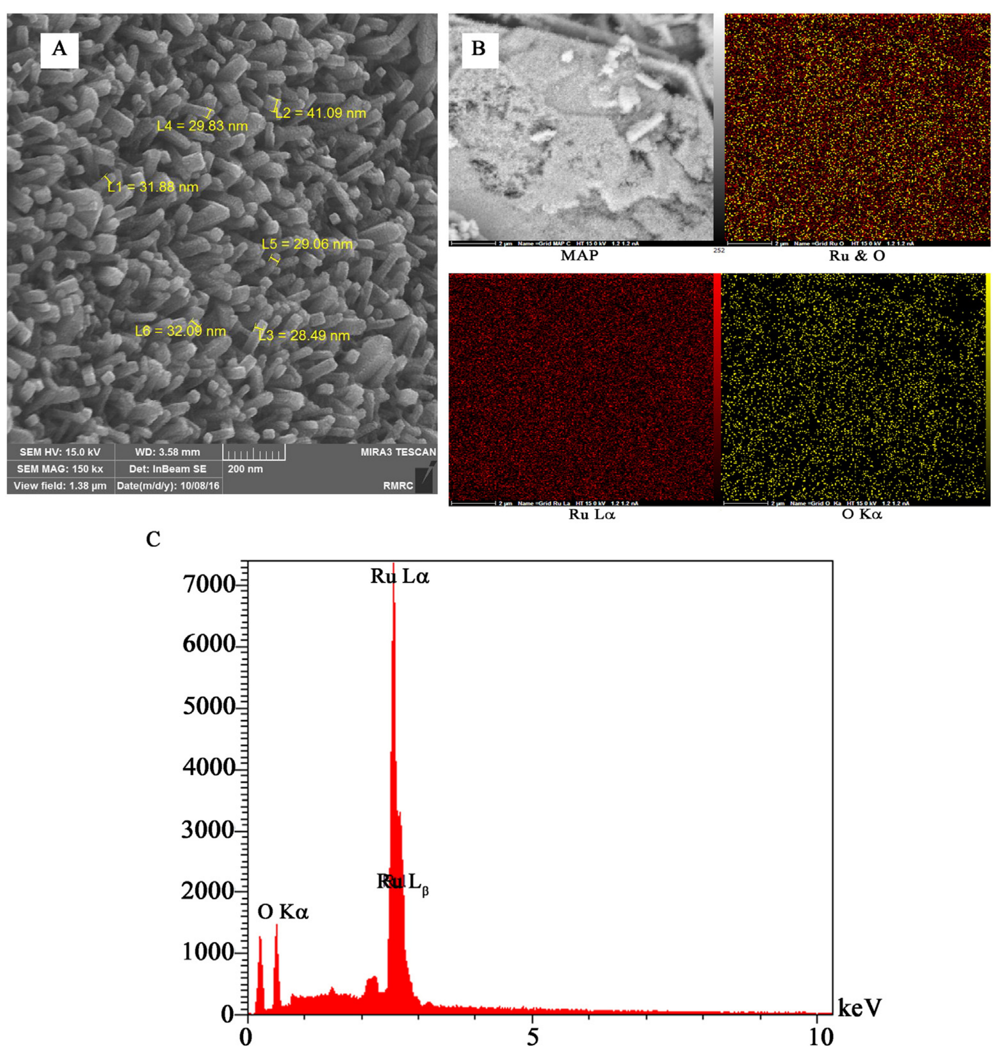

Fig. 1. A) SEM image of as-synthesized RuO_2/NR. B) Elemental analysis (map analysis) of as-synthesized RuO_2/NR. C) EDAX analysis of RuO_2/NR.