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Improve the performance of carbon paste electrodes for determination of dobutamine using $MnZnFe_2O_4$ nanoparticles and ionic liquid

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ABSTRACT

Dobutamine (DB) is a commonly used drug for treating heart failure specially in coronary care units. In this work, $MnZnFe_2O_4$ nanoparticles were synthesized using chemical co-precipitation method, without subsequent calcination steps in high temperature. A new sensor was prepared for determination of dobutamine by improvement of performance of carbon paste electrode using $MnZnFe_2O_4$ and ionic liquid. Investigation of electrochemical behavior of DB on the modified electrode showed that dobutamine was oxidized in lower potentials and oxidation current was increased dramatically in comparison with unmodified electrode. The sensor had two linear dynamic range in the range of 4.0–148.0 and 148.0–740.0 µmol/L DB with limit of detection 1.0 µmol/L DB. The proposed method was successfully applied to determine DB in urine and pharmaceutical samples.

1. Introduction

Dobutamine is a sympathomimetic drug that combines with beta-adrenoceptors relatively selective and is primarily used for short treating heart failure caused by surgery or heart disease. The effect of dobutamine in the heart is similar to that of isoproterenol. Dobutamine is normally administered by intravenous infusion because it has little bioavailability when administered orally. The major side effects of dobutamine are commonly including elevation of systolic blood pressure, tachycardia, ectopic beats, angina, and palpitations [1].

The most commonly employed method for the determination of dobutamine is reverse phase high performance liquid chromatography with fluorescence detector [2–5] or photo diode array [6]. In these methods, dobutamine extracts from biological fluids by liquid–liquid extraction or solid phase extraction. In addition, several other methods have been applied for determination of dobutamine including enzymatic catalytic spectrofluorimetry [7], flow injection chemiluminescence [8] and spectrophotometric method [9].

Dobutamine has a catecholamine group that is readily oxidized at electrodes. Zhang has been reported an electrochemical method for determination of dobutamine based on glassy carbon that modified by Poly(Acridine Orange) film. Catalytic interface was constructed on the electrode by electropolymerization of Acridine Orange. Dobutamine was adsorbed on the modified electrode, and then cyclic voltammetry was used for determination of dobutamine. In this method, after each process, the surface must be renewed by scanning potential [10].

In electrochemical methods several kinds of nano compounds were applied for modification and improving performance of electrodes, including metal or metal oxide nanoparticles [11], carbon nano compounds such as carbon nanotubes and graphene [12]. It is believed that these materials increase active surface area and promote electron transfer between the electro active species and the electrode [13–20].

In this work $MnZnFe_2O_4$ nanoparticles was synthesized without subsequent calcination steps in high temperature and they were applied for modification of carbon paste electrode. In addition, adding an ionic liquid to the structure of carbon paste can increase electrical conductivity of electrode. Accordingly, 1-butyl-3-methylimidazolium hexafluorophosphate was used in this work to preparation of carbon paste. Then the modified electrode (IL/NP/CPE) was used to electrochemical study and determination of dobutamine.

2. Experimental

2.1. Apparatus and chemicals

All voltammetric measurements were carried out by SAMA 500 potentiostat/galvanostat (Isfahan, Iran). A conventional three-electrode cell assembly was employed for the experiments in a 50 mL glass cell containing an Ag/AgCl electrode as reference electrode, a platinum wire as counter electrode and IL/NP/CPE as work-

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ing electrode. All of the potentials were measured and reported *vs.* Ag/AgCl reference electrode. The pH of the solutions was controlled with a Metrohm pH meter (model 827). Bruker (model D8 ADVANCE, Cu Kα wavelength: 1.54184 Å, Filter: Ni) X-ray powder diffractometer was applied to obtain X-ray diffraction spectrum of synthesized nanoparticles.

All chemicals were purchased in the analytical grade. Dobutamine hydrochloride (≥98%) and 1-butyl-3-methylimidazolium hexafluorophosphate (ionic liquid) was purchased from Sigma. Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol/L) solutions (PBS) with different pH values were used.

2.2. Synthesis of nanoparticles

$MnZnFe_2O_4$ nanoparticles were synthesized using chemical co-precipitation method, without subsequent calcination steps in high temperature. For this purpose, four solutions of $MnCl_2$ (0.05 M), $ZnCl_2$ (0.05 M), $FeCl_3$ (0.2 M) and NaOH (0.8 M) were prepared in the double distilled water, under vigorous stirring. At first, the NaOH solution was stirred constantly and heated to 80 °C. Then the solutions of manganese, zinc and ferric chlorides were mixed together and were heated to 80 °C. Then NaOH solution was added to the mixture and temperature of mixture was kept to 80 °C for 1 h, under vigorous stirring. Under these conditions, the calcination and phase transition were occurred [21–23]. The precipitate is isolated from the solution by several times filtration and washing by double distilled water, and dried at room temperature.

2.3. Preparation of modified electrode

In order to modification of carbon paste electrode, 0.85 g graphite powder, 0.05 g synthesized nanoparticles and 0.1 g 1-butyl-3-methylimidazolium hexafluorophosphate were mixed together well and 1 mL diethylether was added to mixture to get uniform mixture. After evaporation of diethylether, 0.8 g viscose paraffin was added and the mixture was mixed with mortar and pestle to get a soft paste. This paste was put into the glass tube and was compressed by a copper wire from another side of the tube. The copper wire was connected to the potentiostat/galvanostat instrument. To obtain new surface of carbon paste electrode, an excess paste pushed and polished on a weighing paper. In addition, the unmodified electrode was prepared in the same way without adding both modifier (CPE) and tow electrodes were prepared with adding only nanoparticles (NP/CPE) or ionic liquid (IL/CPE) to the mixture of carbon paste.

3. Results and discussion

3.1. Investigation of synthesized nanoparticles

In order to confirm the preparation of nanoparticles, several techniques were applied. The X-ray diffraction of the synthesized nanoparticles has been shown in Fig. 1A. The Miller indices were obtained at (220), (311), (222), (400), (422), (511) and (440) which confirm the formation of $MnZnFe_2O_4$. This pattern is closely adapted with cubic spinel structure of the MnZn ferrite and hematite [24]. In addition the mean crystallite size of $MnZnFe_2O_4$ was calculated to be 8–9 nm using Scherrer equation [25]. The particle size and spherical nanocrystalline structure of particles have been visualized through transmission electron microscope (TEM) in Fig. 1B. Also, the energy dispersive X-ray analysis (EDXA) showed that the synthesized nanoparticles contained Mn, Zn, Fe and O elements (Fig. 1C).

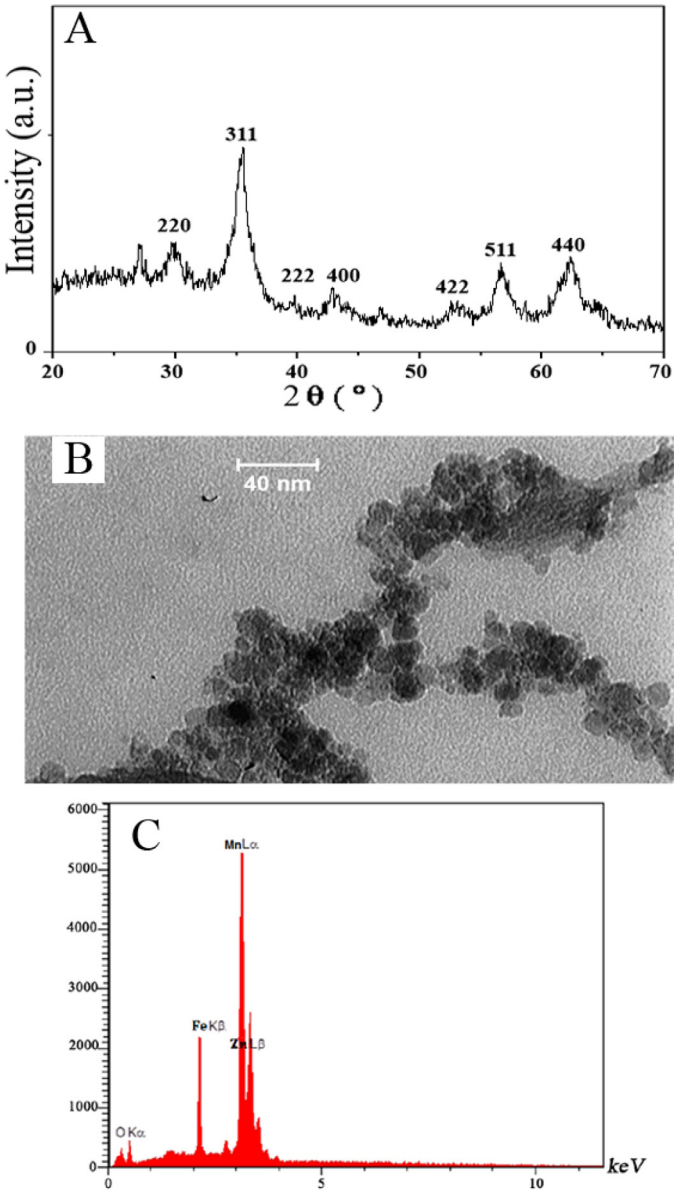

Fig. 1. (A) X-ray diffraction pattern, (B) TEM image and (C) EDXA spectrum of synthesized nanoparticles.

3.2. Electrochemical behavior of DB on modified electrode

To study the effect of pH on the oxidation current of DB at IL/NP/CPE, cyclic voltammograms of 350 µmol/L DB solutions with different pHs were recorded. As can be seen in Fig. 2A, oxidation peak potentials have been shifted to negative potentials with increasing pH of the solution. This effect was due to corporation of proton in the oxidation reaction of DB as predicted by the Nernst equation (Fig. 2B). In addition, when the pH of solution was set to 7.0, maximum oxidation current was obtained and this pH was selected for further experiments.

Fig. 3 shows the effect of modifiers in the oxidation current and potential of 400 µmol/L DB (pH = 7.0). Addition of $MnZnFe_2O_4$ nanoparticles to the carbon paste caused to reduce oxidation potential and to increase oxidation current compared with unmodified carbon paste electrode (Fig. 3b). This effect may be due to addition of activation surface area of electrode in the presence of nanoparticles. Also, addition of ionic liquid to the carbon paste has similar effect by increasing the electrical conductivity of the elec-

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