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$CoFe_2O_4$ nanoparticle/ionic liquid modified carbon paste electrode as an amplified sensor for epirubicin analysis as an anticancer drug

Fatemeh Karimi [a,*], Abdollah Fallah Shojaei [b,*], Khalil Tabatabaeian [b], Shahryar Shakeri [c]

[a] Pardis Campus, University of Guilan, P.O. Box 1841, Rasht, Iran
[b] Department of Chemistry, Faculty of Sciences, University of Guilan, P.O. Box 1914, Rasht, Iran
[c] Department of Biotechnology, Inst. of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran

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ABSTRACT

A suitable amount of $CoFe_2O_4$ nanoparticle ($CoFe_2O_4$/NPs) was used for modification of carbon paste electrode in the presence of paraffin oil and 1,3-dipropylimidazolium bromide (1,3-DPIBr) as binders. The modified electrode showed highly catalytic activity for electro-oxidation of epirubicin in biological condition. $CoFe_2O_4$ nanoparticle were synthesized by co-precipitation method with diameter of ~17.0 nm and characterized with XRD and TEM methods. The chronoamperometry method was used to evaluate diffusion coefficient (D_{app}) of the epirubicin in phosphate buffer solution pH = 7.0. A calibration curve with sensitivity (0.1426 μA/μM) was obtained for epirubicin in the concentration range 0.04–450 μM at a surface of proposed electrode. Finally, the amplified sensor showed good ability of analysis of epirubicin in injection and serum samples.

1. Introduction

Epirubicin is a cancer chemotherapy agent similar to doxorubicin that recommends for treat breast cancer in the combination of other anticancer drugs. Due to low side effect compare to doxorubicin, this drug prescribed for patients with breast cancer that surgery removes the tumor. Nausea or vomiting, low blood counts, and hair loss are the most important side effect of epirubicin. Therefore, the prescribed of this drug in the suitable amount is very important in the treat of breast cancer. To date, many analytical techniques have been developed for the determination of epirubicin in clinical or pharmaceutical samples such as high performance liquid chromatography [1,2] and electrochemical methods [3–6].

Electrochemical methods have a more attention compare to HPLC methods for analysis of clinical or pharmaceutical samples due to simple operation and fast response [7–12]. On the other hand, electrochemical methods didn't used organic and inorganic solvents and are safe methods compare to HPLC method [13–20]. Therefore, electrochemical methods are good choice for analysis of clinical and pharmaceutical samples [21–27]. For improving sensitivity of electrochemical methods, electrochemists were suggested modified electrode as highly sensitive and good selective tools [28–32]. In between, nano-materials such as metal based nanoparticles, carbon nanotubes, conductive polymers, graphene and ionic liquids showed better ability for improving sensitivity and selectivity of electrochemical sensors [33–39]. Coupling of ionic liquids and metal based nanoparticles can be useful for increasing sensitivity of electrochemical sensors and determination of electro-active materials in the nano-molar concentrations [40–44].

In this research, the advantages of using carbon paste electrode modified with $CoFe_2O_4$ nanoparticle and 1,3-dipropylimidazolium bromide ($CoFe_2O_4$/NPs/1,3-DPIBr/CPE) combined with square wave voltammetry (SWV) for the determination of epirubicin in medicinal injections and pharmaceutical serum samples are presented. The $CoFe_2O_4$/NPs/1,3-DPIBr/CPE showed better dynamic range and limit of detection compared to previous electrochemical sensor for analysis of epirubicin (see Table 1). As can be seen, the $CoFe_2O_4$/NPs/1,3-DPIBr/CPE showed better limit of detection compare to references [3, 4 and 6]. Only Wang et al. reported [5] has better limit of detection compare to our suggestion sensor. On the other hand, we suggested sensor showed better linear dynamic range compare to Wang et al. report. Overally, the $CoFe_2O_4$/NPs/1,3-DPIBr/CPE can be suggested as highly sensitive with good linear dynamic range for analysis of epirubicin.

2. Experimental

2.1. Chemicals and apparatus

Iron(III) chloride hexahydrate, cobalt(II) nitrate hexahydrate, epirubicin, graphite powder, sodium hydroxide and paraffin oil were purchased from Sigma-Aldrich. Other compounds were

* Corresponding authors.
E-mail addresses: fkm024@gmail.com (F. Karimi), a.f.shojaie@guilan.ac.ir (A.F. Shojaei).

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Table 1
The analytical data reported by some different electrochemical sensors for epirubicin analysis.

Electrode	pH	Linear dynamic range (μM)	Limit of detection (μM)	Ref.
Glassy carbon electrode	7.0	0.08–10.0	0.02	[3]
Screen printed electrode	4.5	0.005–0.2	0.002	[4]
Screen printed electrode	4.5	0.0184–2.35	0.00147	[5]
Boron-doped diamond electrodes	1.0	0.197–73.5	0.134	[6]
Carbon paste electrode	7.0	0.04–450.0	0.01	This work

purchased from Merck Company. Voltammetric investigations were done by a potentiostat/galvanostat system (Autolab PGSTAT 12). EQuniox 3000 diffractometer was used for characterization of $CoFe_2O_4$/NPs.

2.2. Synthesis of $CoFe_2O_4$/NPs

Chemical co-precipitation technique using iron chloride and cobalt(II) nitrate was utilized for synthesis of $CoFe_2O_4$/NPs. The cobalt(II) nitrate and iron chloride(III) solutions were mixed with the molar ratio of Fe to Co as 2:1 in 150 mL distilled water. The precipitating agent used was 3.0 M sodium hydroxide (25 mL). Metal ions and precipitating agents were added dropwise from two separate burettes into a reaction vessel with 250 mL of distilled water until it reaches uniform particle size distribution under stirrer condition of 700 rpm. Colloidal solution was ultrasonicated at 150 W at a temperature of 90 °C for 2 h. After reaction, the colloidal solution was cooled to room temperature and it was filtered and leached and washed permanently in distilled water until precipitate pH reaches 7.0. Thereafter, $CoFe_2O_4$/MNPs was dried at temperature of 100 °C for 24 h.

2.3. Fabrication of $CoFe_2O_4$/NPs/1,3-DPIBr/CPE

$CoFe_2O_4$/NPs/1,3-DPIBr/CPE was fabricated by mixing 0.15 g of 1,3-DPIBr, 0.75 g of the paraffin, 0.1 g of $CoFe_2O_4$/NPs, and 0.90 g of graphite powder. After mixing of compounds, the obtained paste input in end of glass tube and copper wire was used for electrical contact.

2.4. Real sample preparation

In injection sample and pharmaceutical serum were used as real samples without any pretreatment. The standard addition method was used for analysis of epirubicin in real samples.

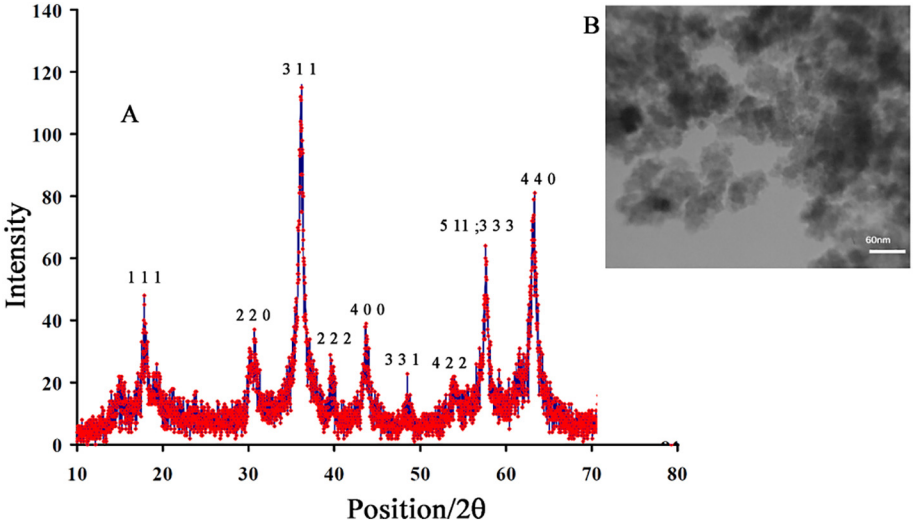

Fig. 1. XRD pattern (A) an TEM image (B) $CoFe_2O_4$ nanoparticle.

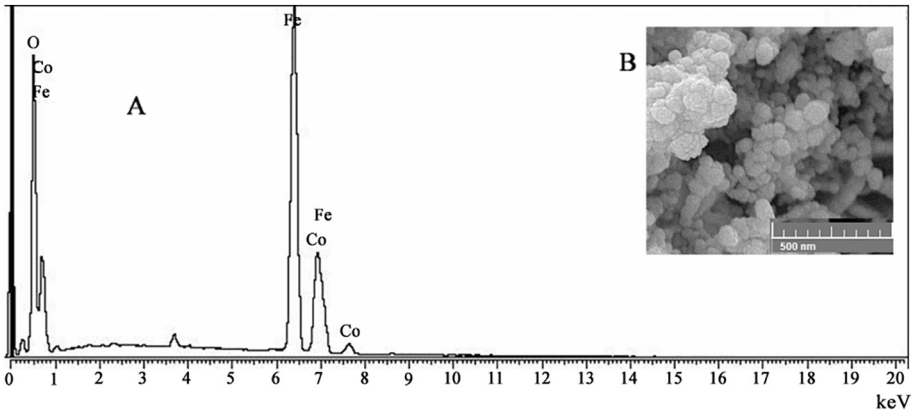

Fig. 2. A) EDAX analysis data for $CoFe_2O_4$ nanoparticle. B) SEM image of $CoFe_2O_4$ nanoparticle.