Materials Science and Engineering C 76 (2017) 88–93

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Template synthesis of maghemite nanoparticle in carboxymethyl cellulose and its application for electrochemical cabergoline sensing

F. Hasanpour *, M. Taei, S.H. Banitaba, M. Heidari

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

ARTICLE INFO

Article history:
Received 4 September 2016
Received in revised form 26 December 2016
Accepted 24 February 2017
Available online 28 February 2017

Keywords:
Cabergoline
Carboxymethyl cellulose/maghemite nanocomposite
Modified carbon paste electrode
Electrochemical determination

ABSTRACT

Maghemite (γ-Fe_2O_3) nanoparticles were produced via coprecipitation onto carboxymethyl cellulose matrix based templates followed by calcination. The resulting maghemite nanoparticles were characterized by Fourier transform infrared spectra, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The magnetization measurement of as-synthesized γ-Fe_2O_3 displayed superparamagnetic characteristics at room temperature. Then, a novel maghemite nanoparticles carbon paste modified electrode was developed for determination of cabergoline. The modified electrode has an outstanding catalytic effect on the oxidation current of cabergoline and the mechanism was studied using cyclic voltammetry. The oxidation peak current was proportional to the concentration of cabergoline from 1×10^{-7} to 3.5×10^{-5} mol L^{-1} with a detection limit of 3×10^{-8} mol L^{-1} at signal to noise ratio of 3. The proposed method was examined as a selective, simple and precise method for voltammetric determination of cabergoline in plasma and pharmaceutical samples.

1. Introduction

Cabergoline (Scheme 1), a strong prolactin inhibitor in humans, is used for the treatment of prolactinoma disorders in prolactin-secreting tumors and Parkinson's disease [1,2]. Cabergoline is also a *dopamine* receptor agonist which is the hopeful candidates to recover outcome of nonremitting depression patients [3]. Cabergoline exhibits poor UV absorbance and fluorescence, as well as little thermal stability and low volatility; as a result some analytical methods such as high-performance liquid chromatography with UV or fluorescence detector and gas chromatographic techniques were not convenient for its sensitive determination [4]. Many techniques have been developed and validated for determination of cabergoline such as high-performance liquid chromatographic [5] spectrophotometry [6] electrospray ionization tandem mass spectrometry [7], liquid chromatography–tandem mass spectrometry [8] and electrochemical methods [9,10]. Among these techniques, electroanalytical methods characterized by instrumental simplicity, moderate cost, reasonable accuracy, precision, and speed [11–14]. The structure of cabergoline contains indole moiety consisting of a benzene ring and a pyrrole ring. The indole derivatives have the potential for providing redox reactions [15,16]. In recent years, chemically modified electrodes have been developed in electrochemical techniques [17–24]. An important motivation for electrode surface modification is electrocatalysis of the electrode reaction of an analytically desired substrate [25–33]. Magnetic nanoparticles have been extensively used to modify the surface of electrodes in electrochemical sensors because they can enhance the electrochemical signals. Iron oxide nanoparticles are one of the most important components of these propose owing to low toxicity, easy preparation, good electrical conductivity large surface area and unique magnetic properties. Among the iron oxide phases such as FeOOH, $Fe(OH)_3$, Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3, only the Fe_3O_4 and γ-Fe_2O_3 have magnetic property. However, the main advantage of maghemite over magnetite is better chemical stability. Maghemite (γ-Fe_2O_3) nanoparticles (NPs), iron oxide with inverse–spinel type; is receiving growing attention in nanoscience and nano technology because of magnetic properties, biocompatibility, chemical stability and low cost [34,35]. Despite of the attractive feature of maghemite, some challenge related to the aggregation behavior of magnetic nanoparticles will be remain which lead to enlargement of nanoparticle size to several microns. Both the physical and the chemical properties of magnetic nanoparticles depend on their nanometric dimension and differ from those of the own bulk properties. The use of some polymeric matrices can prevent nanoparticle aggregations and also control their size [36,37]. Cellulose is an attractive polymeric substrate for the immobilization of metal nanoparticles because it possesses six hydroxyl groups per each repeating cellobiose unit. The main characteristics of cellulose, which acts as a useful matrix for the synthesis of nanoparticles is its porous texture and wider decomposition temperatures [38,39]. Formation of nanoparticles on the surface of cellulose fibers can generate uniform metal nanoparticles. The present work describes the synthesis of maghemite/carboxymethyl cellulose (CMC) nano composite with incorporating magnetic nanoparticles inside a CMC polymer. After the formation of γ-Fe_2O_3 nanoparticles in

* Corresponding author.
E-mail address: f.hasanpour@pnu.ac.ir (F. Hasanpour).

http://dx.doi.org/10.1016/j.msec.2017.02.128
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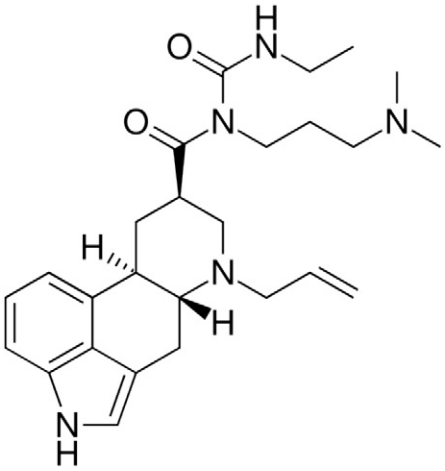

Scheme 1. The structure of cabergoline.

carboxymethyl cellulose, the matrix was removed with calcinations resulting in highly porous γ-Fe_2O_3 nanoparticles. Then γ-Fe_2O_3 NPs modified carbon paste electrode (CPE) was fabricated as an efficient catalyst for the electro oxidation and determination of cabergoline in plasma and pharmaceutical samples.

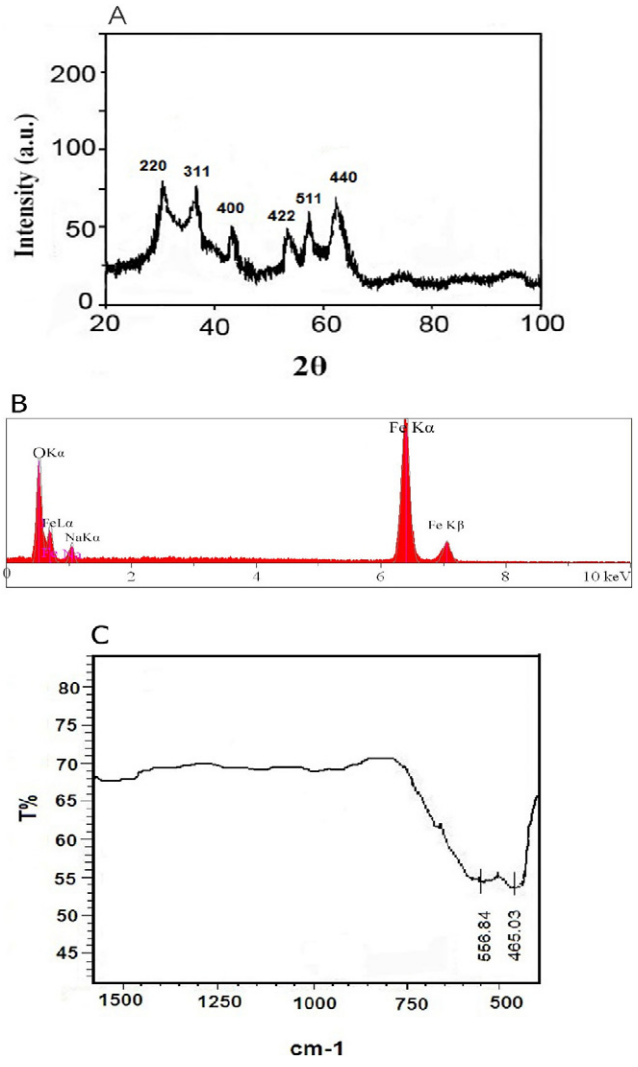

Fig. 1. XRD patterns of the synthesized γ-Fe_2O_3 nanoparticles (A); The corresponding EDX spectrum taken from the whole area of (A) and FT-IR absorption spectra of γ-Fe_2O_3 nanoparticles (C).

2. Experimental

2.1. Apparatus

The electrochemical experiments were performed using an electrochemical system comprising the Autolab PGSTAT101with NOVA software (Ecochemie, Utrecht, The Netherlands), and the three-electrode cell assembly consist of an Ag/AgCl reference electrode, a platinum

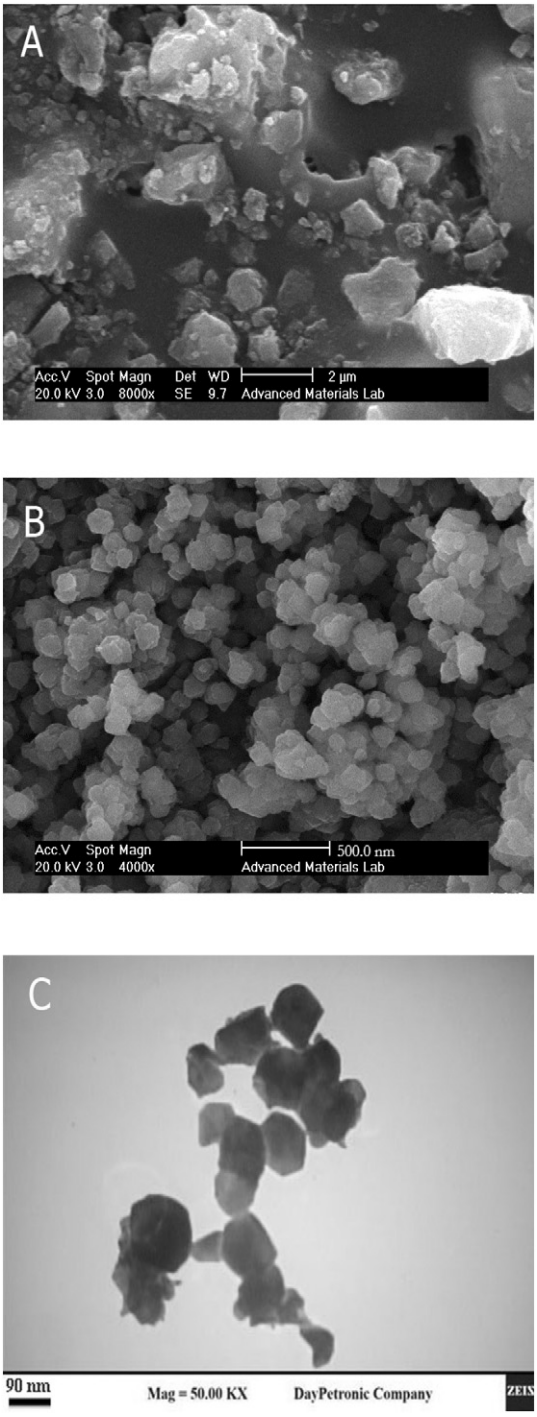

Fig. 2. FESEM (A) before; (B) after calcination process of γ-Fe_2O_3 synthesis and (C) TEM image of the γ-Fe_2O_3nanoparticles.