



ELSEVIER

Contents lists available at SciVerse ScienceDirect

Talanta

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

Electrodeposited apatite coating for solid-phase microextraction and sensitive indirect voltammetric determination of fluoride ions



Yuehong Mao, Yufei Chen, Lin Chu, Xiaoli Zhang*

School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:

Received 8 March 2013

Received in revised form

6 June 2013

Accepted 10 June 2013

Available online 15 June 2013

Keywords:

Electrodeposition

Apatite coating

Solid-phase microextraction

Fluoride ions

Indirect determination

ABSTRACT

Electrodeposition was used to prepare a new solid phase microextraction (SPME) coatings. Two apatite SPME coatings, dicalcium phosphate dihydrate (DCPD or brushite) and hydroxyapatite (HAP) were validly and homogeneously one-step electrodeposited on glassy carbon electrode (GCE) under different conditions. The coatings were characterized by XRD, FTIR, SEM, CV and EIS. The apatite SPME coatings showed excellent and selective adsorbability to fluoride ions. A novel indirect voltammetric strategy for sensitive detection of fluoride was proposed using $K_3Fe(CN)_6$ as indicating probe. The detection principle of fluoride ions was based on the increment of steric hindrance after fluoride adsorption, which resulting in the decrease of the amperometric signal to $Fe(CN)_6^{3-}$. The liner ranges were 0.5–20.0 $\mu\text{mol/L}$ for *n*-DCPD/GCE with the limit of detection of 0.14 $\mu\text{mol/L}$ and 0.1–50.0 $\mu\text{mol/L}$ for *n*-HAP/GCE with the limit of detection of 0.069 $\mu\text{mol/L}$, respectively. The developed method was applied to the analysis of water samples (lake, spring and tap water) and the recovery values were found to be in the range of 90–106%.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Solid-phase microextraction (SPME), developed by Pawliszyn and co-workers [1], is a simple, rapid and solvent-free preparation technique since it has been introduced in the early 1990s. Hence the SPME has been well developed [2]. The key of the technique is the extraction fiber [3]. In this regard, different coating techniques have been introduced including pasting with adhesives, electrochemical polymerization or deposition, direct pasting, chemical corrosion, and the sol-gel technique [4]. Among all the techniques, electrodeposition offers important advantages, such as a rigid control of the film thickness formed, uniformity and fast deposition rate.

Fluoride is an essential constituent for animals including humans [5]. However, the total amount ingested or its concentration in drinking water must be within certain limits [6]. It is very important for us to detect fluoride ions. At present, the most popular technique for fluoride ions detection is fluoride ion selective electrode (ISE) [7], fluorescence analysis [8], gas chromatography and liquid chromatography [9]. There are some limitations in these methods. The response of ISE needs long time for signal obtaining because it takes much time for equilibrium establishment. Fluorescence analysis is often associated with organic chemicals which are environment-unfriendly and chromatography is expensive. Therefore, a reliable, simple, fast,

sensitive, and cost-effective method for fluoride ions detection is asked to propose.

In recent years, removal of fluoride from aqueous solution by adsorption is a simple and attractive strategy due to its high efficiency and easy handling [10]. Various apatite materials were found to be a suitable sorbent for fluoride because of their low costing, availability and high adsorption efficiency as previously reported in the literature [11]. The apatite materials can be fabricated by employing many chemical-based processing routes for example solid-state reaction, sol-gel technique, biosynthesis route, wet chemical route, chemical precipitation, hydrothermal reaction, microwave heating, microemulsions and recently electrodeposition method [12–15]. One-step electrodeposition of apatite [16] has attracted significant interest for sensing applications owing to their excellent stability and good biocompatibility [17].

Herein, we attempted to use apatite coatings prepared by electrodeposition as SPME fibers for fluoride extraction. The apatite SPME coatings (DCPD and HAP) were directly electrodeposited onto GCE from the electrolyte solution containing $Ca(NO_3)_2 \cdot 4H_2O$ – $NH_4H_2PO_4$ via a constant potential of -1.0 V (vs. SCE) for 500 s. The resulting SPME fibers displayed selective and particular adsorbability to the fluoride ions. A novel sensitive indirect voltammetric determination method of fluoride ions was proposed using $K_3Fe(CN)_6$ as indicating probe. The introduction of indicating probe solved the problem that the direct oxidation–reduction of fluoride ions is difficult. The experiment mode was based on the change of current signal before and after fluoride extraction, and a new method for detecting fluoride ions was

* Corresponding author. Tel.: +8653188361318; fax: +8653188564464.
E-mail address: zhangxl@sdu.edu.cn (X. Zhang).

developed. The apatite was characterized by XRD, FTIR, SEM, CV and EIS. Analytical performances of the proposed SPME approach were tested. Finally, three real water samples were employed to this method with satisfactory results.

2. Experimental

2.1. Apparatus

A CHI 800 electrochemical analyzer (Shanghai Chenhua Instrument Company, China) was used to perform electrode characterizations and voltammetric measurements. A conventional three-electrode system including a glassy carbon electrode (GCE, 3 mm diameter) or modified GCE as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode was used in this work.

2.2. Reagents

Sodium fluoride was obtained from Shanghai Xinhua Chemical Reagent Corporations Ltd. (China). Calcium nitrate and ammonium dihydrogen phosphate was obtained from China National Pharmaceutical Group Corporations Ltd. (China). $K_3Fe(CN)_6$ was purchased from Sinopharm Chemical Reagent Beijing Corporations Ltd. (China). All the reagents were of analytical reagent grade and used as received. Electrolytic solutions were prepared using ultrapure water (Ulupure, Chengdu, China, 18.2 M Ω resistivity) and deaerated with nitrogen. All electrochemical measurements were conducted in deaerated solutions. The experiments were performed at room temperature, 298 K.

2.3. Preparation of the apatite SPME coating

The GCE was polished repeatedly using alumina powder (0.50, 0.30 and 0.05 μ m) and thoroughly cleaned. The GCE was immersed into the electrolyte containing 0.23 mol/L $Ca(NO_3)_2 \cdot 4H_2O$ and 0.14 mol/L $NH_4H_2PO_4$ (deoxygenization for 1 min in nitrogen flow, pH 3.0). The electrodeposition was conducted at -1.0 V for 500 s with the magnetic stirring controlled at 60 rpm to keep the concentration uniform. The resulting electrode, *n*-DCPD SPME coating modified GCE, was activated by several successive cyclic voltammetry from -0.2 to 1.4 V with a scan rate of 50 mV/s in phosphate buffer (pH 7.0) until a steady voltammogram was obtained. To obtain the *n*-HAP SPME coating, steps were all the same to the former except that the pH value of the electrolyte was adjusted to 7.0 with ammonia before electrodeposition. They were stored in a refrigerator (4 °C) when not used.

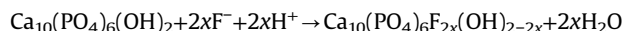
2.4. Extraction and detection for fluoride ions

First, the apatite SPME coating modified electrode (*n*-DCPD/GCE or *n*-HAP/GCE) was immersed into the solution of fluoride ions for extraction (through an accumulation of 10 min on open circuit). After being taken out, the *n*-FD/GCE or *n*-FHA/GCE (after *n*-DCPD/GCE or *n*-HAP/GCE extracting fluoride ions) was obtained. Subsequently, the electrode with fluoride ions (*n*-FD/GCE or *n*-FHA/GCE) was performed the stripping voltammetric detection in another supporting electrolyte of KCl containing $K_3Fe(CN)_6$ as indicator. The voltammogram was recorded from 0 to 0.5 V and the peak height was measured as a signal (*I*). The corresponding voltammogram of blank modified electrode (before extraction) was recorded and the peak height was marked as I_0 . The quantification of fluoride was achieved based on the change of current signal ΔI ($\Delta I = I_0 - I$) with the fluoride ions concentration.

3. Results and discussion

3.1. X-ray diffraction, fourier transform infrared spectrum and scanning electron microscopy

The prepared apatite coating was characterized by X-ray diffraction (XRD, Rigaku D/MAX-rA). The XRD data were collected from 10° to 70° using Cu $K\alpha$ radiation at 40 kV and 40 mA. The crystalline phases were determined from a comparison of the XRD patterns with the JCPDS powder diffraction file. Fig. 1 represents XRD patterns of the DCPD, FD, HAP, and FHA. For DCPD, the most prominent peak, which was situated at an angle of $2\theta = 11.7^\circ$, corresponded to the DCPD (0 2 0) peak. The XRD results also showed typical crystallized peaks of DCPD at $2\theta = 20.9^\circ$ and $2\theta = 29.3^\circ$. All the well-defined diffraction peaks in graph were identical to the pattern of JCPDS card 09–0077, confirming the formation of DCPD on the surface of GCE. After extracting fluoride 10 min on open circuit, *n*-FD/GCE was obtained. For FD, there were some significant changes in the scalar and location of diffraction peaks, for instance, crystal faces (0 2 1), (0 4 1) of the brushite peaks were not found in spectrum. Only amorphous particles were possible to see. The results represented that fluoride ion had been inserted into DCPD and damaged its structure. As presented in XRD patterns of HAP and FHA, the most intensive peaks were the (3 0 0), (2 1 1), and (0 0 2) peaks. In addition, there were weaker peaks, (3 1 0), (2 2 2), (2 1 3) and (3 2 3) according to the PDF data base. For the FHA, almost all the crystal diffraction remained by comparison with the HAP, indicated that there were no significant changes in the crystal shape. However, the diffraction intensities of three peaks around $2\theta = 32^\circ$ were decreased obviously after the fluoride ions extraction. Many literatures [10,11,18] reported that hydroxyapatite had the sorption behavior for fluoride ions. This behavior could be attributed to the presence of OH^- that might compete with F^- for the sorption sites in the sorbent material [18,19], the possible reaction process of F^- at the *n*-HAP/GCE was as followed in our work:



As for the decrease of the diffraction intensity, the reason might be that the excess fluoride ions were full of the nano-porous

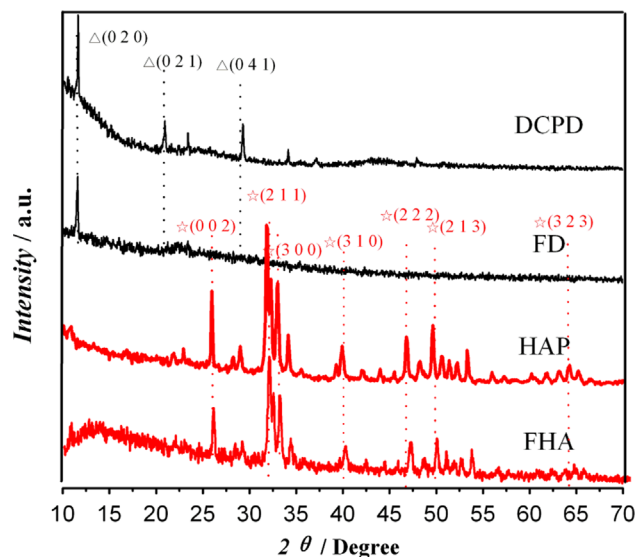


Fig. 1. XRD of *n*-DCPD, *n*-HAP, *n*-FD and *n*-FHA. Symbol Δ was for *n*-DCPD or *n*-FD. Symbol \star was for *n*-HAP or *n*-FHA. Two apatite SPME coatings were obtained by electrodeposition at -1.0 V for 500 s. The initial concentration of fluoride ions for extraction was 40.0 μ mol/L.

Download English Version:

<https://daneshyari.com/en/article/7682881>

Download Persian Version:

<https://daneshyari.com/article/7682881>

[Daneshyari.com](https://daneshyari.com)