Food Chemistry 121 (2010) 580–584

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

Electrocatalysis and sensitive determination of Sudan I at the single-walled carbon nanotubes and iron(III)-porphyrin modified glassy carbon electrodes

Yunhua Wu *

Key Lab for Biotechnology of National Commission for Nationalities, College of Pharmacy, The South Central University for Nationalities, Wuhan 430074, PR China

ARTICLE INFO

Article history:
Received 31 January 2009
Received in revised form 2 November 2009
Accepted 13 December 2009

Keywords:
Iron-porphyrin
Single-wall carbon nanotubes
Sudan I
Catalytic reduction
Food analysis

ABSTRACT

Iron-porphyrin (5,10,15,20-tetraphenyl-21H, 23H-porphine iron(III) chloride) was used in combination with single-wall carbon nanotubes (SWNTs) to modify a glassy carbon electrode (GCE). The electrochemical behavior of Sudan I on the iron-porphyrin-SWNT-DMF (*N*,*N*-dimethylformamide) modified GCE was studied by the cyclic voltammetry and square wave voltammetry. In pH 7.0 Tris–HCl buffers, Sudan I has a sensitive catalytic reduction peak at −0.08 V on the iron-porphyrin-SWNT-DMF modified GCE. Using square wave voltammetry, the linear relationship of Sudan I is 5.03×10^{-8} mol L^{-1}–2.01×10^{-6} mol L^{-1} with the tropics equation: $\Delta_{iP} = 3.40C + 3.43 \times 10^{-6}$, and the detection limit is 1×10^{-8} mol L^{-1}. And the iron-porphyrin-SWNT-DMF modified GCE was applied successfully in the determination of Sudan I in real samples.

1. Introduction

The lipophilic Sudan I (1-phenylazo-2-naphthol) is a synthetic azo-colorant which has been widely used as a coloring agent in chemical industries and an additive in foods in daily life, particularly in those containing chilli powders, because of their intense red–orange color (He et al., 2007) However, azo-colorants are biologically active through their metabolites and they have been said to associate with increasing occurrence of bladder cancer in textile and leather dyers, painters and hairdressers (Mejia, Ding, Mora, & Garcia, 2007). So Sudan I at any level is not safe for the human beings and has been classified by the International Agency for Research on Cancer (IARC) as a kind of carcinogen. Due to its cancerogenity, any national and international food regulation act does not permit the use of Sudan I as food-additives (Zhang et al., 2007). On this point, developing a sensitive, rapid and convenient method for the determination of Sudan dyes is of great importance and interest.

Until now, the usually proposed methods for the determination of Sudan I in foodstuffs were established on the high performance liquid chromatography (HPLC) (Cornet, Yasmine, Goedele, Loco, & Degroodt, 2006; Ertas, Özer, & Alasalvar, 2007) or HPLC-MS (Calbiani et al., 2006; Tateo & Bononi, 2004) due to their high sensitivity and excellent selectivity. Otherwise, some electrochemical method dealing with measurement of Sudan I was also reported. Sudan I was determined based on its reduction at an electrochemically activated glassy carbon electrode (Du, Han, Zhou, & Wu, 2007). A linear relationship between the reduction current and concentration of Sudan I was obtained over the range from 2.4×10^{-6} mol L^{-1} to 1.8×10^{-5} mol L^{-1} with the detection limit to be about 7.1×10^{-7} mol L^{-1}. Wu's group has established electrochemical methods to detect Sudan I in food samples using modified electrodes based on its oxidation (Lin, Li, & Wu, 2008; Tian, Li, & Wu, 2008). The electrochemical oxidation of Sudan I at a montmorillonite calcium modified carbon paste electrode by cycling the potential between 0.30 and 1.00 V was investigated (Lin, Li, & Wu, 2008). Sudan I yielded a sensitive oxidation peak at 0.65 V. The oxidation peak current is proportional to the concentration of Sudan I over the range from 2.01×10^{-7} mol L^{-1} to 4.03×10^{-6} mol L^{-1}, and the limit of detection is 8.06×10^{-8} mol L^{-1} under 2 min accumulation. The multi-wall carbon nanotube film-modified glassy carbon electrode was also used to determine Sudan I (Tian et al., 2008). The oxidation peak of Sudan I located at 0.68 V by cycling the potential between 0.10 and 1.00 V. The linear range is over the range from 4.031×10^{-8} mol L^{-1} to 4.03×10^{-6} mol L^{-1}, and the limit of detection is 2.01×10^{-8} mol L^{-1} after 3 min accumulation. A method has been reported for dealing with Sudan isomers determination by HPLC separation and electrochemical detection at glassy carbon and carbon nanotube-ionic liquid gel modified electrodes (Chailapakul et al., 2008). A well-resolved oxidation wave of Sudan I was observed at approximately +0.74 V at the MWNTs-ILGel/GC electrode during the scan potential between 0.00 and 1.40 V. The linear range of Sudan I was over the range from 2.031×10^{-8} mol L^{-1} (0.005 ppm) to 6.03×10^{-5} mol L^{-1} (15 ppm), and the limit of detection is 4.02×10^{-9} mol L^{-1} (0.001 ppm). However, to the best

---

* Tel.: +86 27 6113 4047; fax: +86 27 6784 2689.
E-mail address: yunhuawu@yahoo.com.cn (Y. Wu)

0308-8146/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2009.12.051

of our knowledge, electrochemical determination of Sudan I using iron-porphyrin modified electrodes based on its catalytic reduction has not been reported.

Carbon nanotubes (CNTs) are kinds of porous nanostructure of carbon materials, possessing properties such as high electrical conductivity, high surface area, chemical stability and significant mechanical strength (Inagaki, Kaneko, & Nishizawa, 2004). They can be used to promote electron transfer reactions when used as electrode materials in electrochemical devices (Yang, Chen, Xue, Biris, & Zhao, 2005). Iron-porphyrin plays an important role in several nature processes and especially in the human body (Alberts et al., 1994). Due to electrochemical reversibility of iron-porphyrin derivatives, these compounds have been widely applied in catalytic systems (Serra, Docal, & Gonsalves, 2005). In this paper, an electrochemical sensor was constructed by modifying a glassy carbon electrode with SWNTs and iron(III)-porphyrin and the sensor was used for electrocatalytic reduction of Sudan I. Due to the excellent electrocatalytic ability of iron(III)-porphyrin and the unique physiochemical properties of SWNTs , the sensor exhibits an excellent ability toward electro-reduction of Sudan I. And this sensor was applied in the determination of Sudan I.

2. Experimental

2.1. Chemical and reagents

The single-wall carbon nanotubes (SWNTs, obtained from Timenano Co., Chengdu, China, purity $\geqslant$ 99wt%) were synthesized by a catalytic pyrolysis method. Iron-porphyrin: 5,10,15,20-tetraphenyl-21H, 23H-porphine iron(III) chloride was from Sigma and used without further purification. Sudan I (1-[(2,4-dimethylphenyl)azo]-2-naphthalenol), was purchased from Aldrich. 0.10 mg mL^{-1} (4.02×10^{-4} mol L^{-1}) stock solutions of Sudan I was directly prepared in ethanol, and stored at 4 °C in the dark. All the chemicals were of analytical-reagent grade unless otherwise stated and used directly without further purification. The water used in this work is re-distilled. The supporting electrolyte was 0.1 mol L^{-1} Tris–HCl buffers and the pH was adjusted with NaOH or HCl.

2.2. Apparatus

All electrochemical measurements were performed with a model CHI660C electrochemical workstation (CHI Instruments, Chenghua Instrument Co., Shanghai, China) controlled by a personal computer. A conventional three-electrode system equipped with a bare GCE or the prepared iron-porphyrin-SWNT-DMF modified GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode, was used for all electrochemical measurements. All pH measurements were made with a pHs-3 digital pH-meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass electrode.

2.3. Fabrication of iron-porphyrin-SWNT-DMF film-modified GCE

The iron-porphyrin-SWNT-DMF film-modified glassy carbon electrode (GCE) was fabricated as follows: Firstly, a 5.0-mg SWNT and 5.0-mg iron-porphyrin were dispersed into 4.0 mL N, *N*-dimethylformamide (DMF) by 20-min ultrasonic agitation to give a homogeneous iron-porphyrin-SWNT-DMF suspension. Secondly, the GCE was mechanically polished with 0.05 μm alumina slurry to a mirror finish, rinsed and sonicated in re-distilled water for 1 min. Finally, the GCE surface was coated with 5.0 μL of the resulting iron-porphyrin-SWNT-DMF suspension and allowed to evaporate water under an infrared lamp. The SWNT-DMF-coated GCE was prepared by the same procedure explained above but without iron-porphyrin.

2.4. Analytical procedure

Unless otherwise stated, 0.1 mol L^{-1} Tris–HCl buffers (pH 7.0) were used as determining medium for Sudan I analysis. The analytical procedure mainly contains two steps: accumulation step and determining step. Firstly, Sudan I was preconcentrated onto the iron-porphyrin-SWNT-DMF modified GCE surface under −0.4 V for 90s stirring. After that, the square wave voltammograms from 0.2 to −0.3 V were recorded, and the reduction peak current at −0.08 V was measured as the analytical signal for Sudan I.

2.5. Sample preparation

2.5.1. Extraction of Sudan I from hot chili powder and sausage

Hot chili powders and sausages were purchased from a local market. Sausages were pound to pieces firstly. 1.00 g of hot chili powder sand sausages pieces were weighed, and ultrasonicated with 20 mL of ethanol for 20 min, respectively. The extraction procedure is repeated three times, each time the liquid phase after filtration was collected in a 100.0 mL volumetric flask and finally diluted to the exact volume with ethanol for measurement.

2.5.2. Extraction of Sudan I from hot chili juice and sauce

A hot chili juice and sauce were obtained from a local market. The hot chili juice and sauce were directly filtrated, and the filtrate was collected for measurement, respectively.

2.5.3. Extraction of Sudan I from ketchup and chaffy dish flovoring

The ketchup and chaffy dish flovoring samples were obtained from a local market. 10.00 g ketchup and chaffy dish flovorings were weighed, and ultrasonicated with 20 mL of ethanol for 20 min, respectively. The mixture was filtrated and the liquid phase was collected in a 100.0 mL volumetric flask. The extraction procedure is repeated three times, and the collected extract was diluted to volume with ethanol for measurement.

3. Results and discussion

3.1. Electrochemical behavior of iron-porphyrin-SWNT-DMF film-modified GCE

Fig. 1 shows the cyclic voltammograms recorded in Tris–HCl buffers (pH 7.0) at SWNT-DMF film-modified GCE (a) and iron-porphyrin-SWNT-DMF film-modified GCE (b). It was observed that in the absence of iron-porphyrin, no redox peaks were observed for SWNT-DMF film-modified GCE in the potential range from −0.6 V to 0.6 V. By contrast, a pair of well-defined redox peaks was clearly seen when the iron-porphyrin was present on the electrode surface. At the scan rate of 150 mV s^{-1} the oxidation peak and reduction peak were located at 0 V and −0.1 V, respectively. The pair peaks was attributed to the Fe(III)/Fe(II) redox couple coordinated in the porphyrinic ring (Murray, 1983). The effect of potential scan rate, ν, on the peak current and peak potential of iron-porphyrin were evaluated by cyclic voltammetry from from 10 mV s^{-1} to 500 mV s^{-1} (Fig. 2). With increasing the scan rate, both peak currents and peak-to-peak separation increase. The anodic and cathodic peak currents are linearly proportional to the root of scan rate ranging from 10 to 500 mV s^{-1}, with the correlation coefficient 0.998 and the intercept of 2.31578×10^{-6}, nearly zero, indicating the redox reaction is a diffusion controlled electrochemical process.