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Electrochemical reduction of C.I. Acid Red 18 on multi-walled carbon nanotubes and its analytical application

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ABSTRACT

The electrochemical reduction of C.I. Acid Red 18 on the surface of multi-walled carbon nanotube-modified glassy carbon electrode was investigated using cyclic voltammetry. A novel, simple, sensitive and inexpensive method for determination of C.I. Acid Red 18 in soft drinks was proposed and the accuracy and reproducibility of this determination method were evaluated. The method was satisfactorily applied for the determination of C.I. Acid Red 18 in soft drinks in the concentration range 3.30×10^{-7}–1.24×10^{-4} M, with a detection limit of 1.65×10^{-7} M.

1. Introduction

C.I. Acid Red 18 (E-124, C.I. 16255) is a synthetic azo food dye that is routinely found in many common food products such as beverages, sweets, dairy produce and bakery products. As the genetic toxicity of some azo dyes has been confirmed [1,2], accurate and reliable methods for the determination of azo dyes in foods are required. Although spectrophotometry [3–6], adsorptive voltammetry [7,8], reversed-phase liquid chromatography (RPLC) [9–11], ion-pair RPLC [12] and capillary electrophoresis [13–18] have been used for the determination of various water-soluble synthetic dyes, many of these methods are time-consuming.

Since carbon nanotubes (CNTs) were discovered in 1991, CNTs have attracted much research attention. The modification of electrode substrates with multi-walled carbon nanotubes (MWCNTs) has been shown to result in enhanced sensitivity, electron-transfer promotion, increased resistance to surface fouling and reduction of over-potential. It has been reported that CNT modified electrodes can be successfully applied in the determination of many organic molecules [19–25].

To the best of our knowledge, the voltammetric determination of C.I. Acid Red 18 using an MWCNT modified glassy carbon electrode (GCE) has not hitherto been reported. This paper concerns the electrochemical reduction of C.I. Acid Red 18 at the surface of a multi-walled carbon nanotube-modified glassy carbon electrode and the development of a simple, rapid and effective cyclic voltammetric (CV) method for the determination of C.I. Acid Red 18 in soft drinks.

2. Experimental

2.1. Chemicals

C.I. Acid Red 18 (E-124, C.I. 16255), C.I. Acid Yellow 23 (E-102, C.I. 19140), C.I. Acid Red 27 (E-123, C.I. 16185), C.I. Food Yellow 3 (E-110, C.I. 15985), C.I. Acid Blue 74 (E-132, C. I. 73015), C.I. Acid Red 51 (E-127, C.I. 45430), and C.I. Acid Blue 9 (E-133, C.I. 42090) were purchased from National Research Center for CRMS (Beijing, China). The purity of C.I. Acid Red 18 was determined by means of melting point, UV–visible, infrared spectra and HPLC: no impurities were found. A 0.0100 M aq solution of C.I. Acid Red 18 was prepared using double-distilled water. The impurities of other dyes were not examined. MWCNTs were purchased from Shenzhen Nanotechnology Port Co. Ltd. (China). 0.2–2.0 g L^{-1} solutions of MWCNTs was prepared in *N*, *N*-dimethylformamide. All other reagents were of analytical grade. 0.1 M phosphate buffer solution was prepared by dissolving 0.1 mol NaCl and 0.1 mol Na_2HPO_4 in 1 L of double-distilled water and adjusting the pH using 6 M aq HCl or 1 M NaOH solution.

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2.2. Instrumentation

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The electrochemical cells consisted of three electrodes, a 3 mm diameter glassy carbon disc electrode and MWCNT composite modified GCE were used as working electrode, a platinum wire served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode.

2.3. Preparation of MWCNTs and modified GCE

The MWCNTs were purified in boiling concentrated nitric acid for 4 h, followed by rinsing with deionized water and drying under ambient atmosphere. Open-end MWCNTs with hydrophilic surface were thus obtained. Before modification, the GCE was polished with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water, and then sonicated in ethanol and doubly distilled water for 10 min, sequentially. The modifier suspension was prepared by dispersing the MWCNTs in 5.0 mL of *N*,*N*-dimethylformamide under sonication for 30 min. The MWCNT modified GCE was prepared by casting 5 μL of the mentioned above black suspension on the GCE surface using a micropipette and left to dry at room temperature. Before the voltammetric measurements, the modified electrode was cycled between −1 and 1 V (scan rate 100 mV s^{-1}) in 0.1 M phosphate buffer solution for several times until acquiring the reproducible responses.

3. Results and discussion

3.1. Electrochemical behavior of C.I. Acid Red 18 at MWCNT/GCE and selected buffer solution

The electrochemical response of C.I. Acid Red 18 at bare GCE and MWCNT/GC electrode in purged N_2 0.1 M phosphate buffer solution of pH 8.3 is shown in Fig. 1. It could be seen that the reduction peak for the C.I. Acid Red 18 at bare GCE and MWCNT/GCE were observed at −0.812 V and −0.670 V, respectively, the reduction potential of C.I. Acid Red 18 at MWCNT/GC electrode shifted to positive potentials, and the peak current increased.

These results indicated that the MWCNT modified electrode promoted the electrochemical reduction of C.I. Acid Red 18 by considerably accelerating the rate of electron transfer. Purified MWCNTs are functionalized with −OH and −COOH, which could interact with hydroxyl and sulfonyl in C.I. Acid Red 18 to form hydrogen bond. The π–π conjugated bonds between MWCNTs and the C.I. Acid Red 18 probable increase reduction current. The MWCNT interface has a large surface area, a great deal of active sites, better conductivity and favorable electrocatalytic power, all of them led to the dissimilar conjugation effect of C.I. Acid Red 18 with the bare electrode interface.

The similar electrochemical behavior for C.I. Acid Red 18 in acetate buffer or Britton–Robinson buffer (pH 8.3) was observed. However, the background current of MWCNT/GC electrode in acetate buffer or Britton–Robinson buffer was great. Therefore, 0.1 M phosphate buffer solution of pH 8.3 was selected.

3.2. Amount of the modifier

The reduction current for C.I. Acid Red 18 at modified electrode can be affected by the amount of MWCNTs on the electrode surface. This can be controlled by using the same volume (5 μL) of the suspensions with the different concentrations of MWCNTs, casted on the surface of GCE. The experiments showed that the reduction peak current for 9.00×10^{-5} M C.I. Acid Red 18 increased quickly by increasing the concentration of MWCNT suspension deposited on the surface of GCE up to 0.8 g L^{-1} (from 0.00 to 0.80 g L^{-1}). Further increase, caused a gradual decrease in the cathodic peak current of C.I. Acid Red 18 with increase in background current. As a result, 5 μL of 0.8 g L^{-1} MWCNT suspension was selected as optimum volume for preparation of the modified electrode.

3.3. Influence of pH

The influence of pH on the electrochemical behavior of C.I. Acid Red 18 was investigated at different pH values in the range of 2.0–10.0. Fig. 2 shows the CVs of 9.00×10^{-5} M C.I. Acid Red 18 on the surface of the modified electrode over the discussed pH range at the scan rates of 100 mV s^{-1}. It was found that the peak potential shifted negatively with pH increasing and a good linear relationship was observed between the *E* and pH values in the range of 2.0–10.0

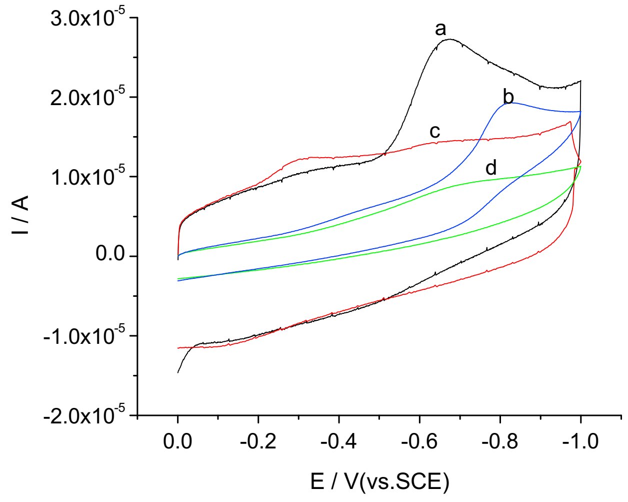

Fig. 1. CVs of 9.00×10^{-5} M C.I. Acid Red 18 at MWCNT/GCE (a) and bare GCE (b); CVs of MWCNT/GCE (c) and bare GCE (d). Scan rate: 100 mV s^{-1}; supporting electrolyte: 0.1 M phosphate buffer with pH 8.3; accumulation volume of 0.8 g L^{-1} MWCNT suspension: 5 μL.

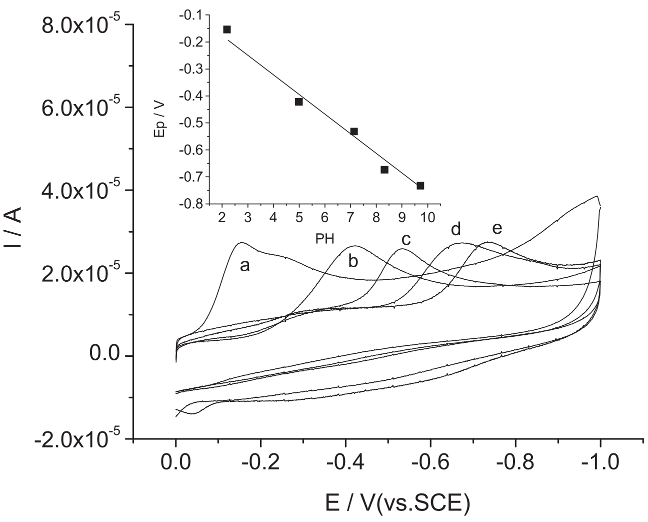

Fig. 2. Influence of pH on the shape of cathodic peak of 9.00×10^{-5} M C.I. Acid Red 18. pH: 2.0 (a), 5.0 (b), 7.0 (c), 8.3(d) and 10.0 (e). Inset: plot of the peak potential against pH. Scan rate: 100 mV s^{-1}; accumulation volume of 0.8 g L^{-1} MWCNT suspension: 5 μL.