Electrochimica Acta 136 (2014) 370–376

Contents lists available at ScienceDirect

Electrochimica Acta

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

Simultaneous Determination of Orange G and Orange II in Industrial Wastewater by a Novel Fe_2O_3/MWCNTs-COOH/OP Modified Carbon Paste Electrode

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ARTICLE INFO

Article history:
Received 26 December 2013
Received in revised form 9 May 2014
Accepted 16 May 2014
Available online 29 May 2014

Key words:
Orange G
Orange II
Oxygen functionalized multi-walled carbon nanotubes
Modified carbon paste electrode
Triton X-100

ABSTRACT

A novel Fe_2O_3 nano-materials/oxygen functionalized multi-walled carbon nanotubes/triton X-100 modified carbon paste electrode (Fe_2O_3/MWCNTs-COOH/OP/CPE) was prepared to simultaneously detect orange G (Or G) and orange II (Or II) by electrochemical methods. Compared with the bare carbon paste electrode (CPE), Fe_2O_3/MWCNTs-COOH/OP/CPE exhibited obvious electrocatalytic activities towards Or G and Or II. Furthermore, the two azo dyes were identified and separated successfully, and were simultaneously determined by the redox peaks in cyclic voltammograms (CVs) and differential pulse voltammogram (DPV) under optimum conditions. In DPV, anodic peak current (Ipa) and concentrations were linearly related well for 0.1-20.0 μM Or G and 0.2-50.0 μM Or II. The limits of detection (S/N = 3) of Or G and Or II were 0.05 μM and 0.1 μM, respectively. Therefore, the electrode is suitable for the determination of Or G and Or II in industrial wastewater due to high sensitivity and selectivity, low detection limit, good reproducibility, as well as easy preparation and regeneration.

1. Introduction

As one-dimensional allotropes of carbon, carbon nanotubes (CNTs) are promising materials for modifying electrodes that are widely applied in both electrochemistry and electroanalysis because of promoting effects on electron transfer, very low background current, simple surface renewal process and high surface area [1,2]. Besides, they have high electrical conductivity, chemical stability and extremely high mechanical strength [3,4]. CNTs combined with metal nano-materials or metal nano-oxides modified electrode have mainly been applied in the fields of clinical assays, materials science, and pharmaceutical analysis [5–8]. However, they are not easily soluble in a large number of solvents [9], thus significantly limiting their manipulations and applications in electroanalysis, especially in the fabrication of CNTs-modified electrodes. Therefore, it is crucial to obtain a homogeneous CNTs suspension.

Surfactant not only enhances the solubilization of organic compounds, but also specifically orients electroactive organic molecules on the electrode surface. Particularly, Triton X-100 (OP) has been widely used in electrochemical analysis as a competent surfactant [10]. Fe_2O_3 nano-oxide, an important material for electrochemically modified electrode, has high biocompatibility, excellent electrontransfer behavior and numerous active reaction sites for chemical reactions. In addition, it can also form covalent bonds and bind materials containing many functionalized groups, such as -COOH, -NH_3, or -CN that are widely used for the production of magnetic materials and catalysts [11].

Among the largest and most versatile classes of dyes with the greatest variety of colors, azo dyes account for more than half of global dye production and have been extensively used by several industries, mainly in textile dyeing by Asian producers [12]. The annual global production of dyes is estimated over 7.0×10^5 tonnes, and about 1.6×10^9 m^3 dye-containing wastewater is generated annually in China [13], leading to serious environment problems that might be carcinogenic and teratogenic for human [14].

Up to now, various methods have been reported for the determination of azo dyes, including ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, liquid chromatography mass spectrometry (LC-MS) and Fourier transform infrared spectroscopy (FT-IR) [15–17]. Nevertheless,

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http://dx.doi.org/10.1016/j.electacta.2014.05.090

these instruments are bulky and need much time to warm-up that restrict online monitoring and in situ testing. Besides, most of the methods require several time-consuming pre-processing steps. In contrast, electrochemical analysis is of significant advantages, such as speediness, simple instrument, miniaturisable consumption of organic solvent, superb sensitivity, and ultrasensitive detection limits. Gan et al. investigated the oxidation of Orange II (Or II) using mesoporous TiO_2 decorated graphene nanocomposite modified GCE and achieved satisfactory detection limits [18]. Other modified electrodes have been developed to determine azo dyes such as tartrazine and brilliant blue [19]. However, determination of Orange G (Or G), especially simultaneous determination of Or G and Or II in environment monitoring, has never been realized by using electrochemical method hitherto.

Thereby motivated, the electrochemical behaviors of Or G and Or II were evaluated in this study by using a Fe_2O_3 nano-materials/oxygen functionalized multi-walled carbon nanotubes/triton X-100 modified carbon paste electrode (Fe_2O_3/MWCNTs-COOH/OP/CPE). The electrochemical responses of Or G and Or II were greatly increased on the surface of Fe_2O_3/MWCNTs-COOH/OP modified electrode. Besides, the modified electrode showed better electrochemical performance toward Or G and Or II in industrial wastewater samples than other working electrodes did with satisfactory recoveries. Being time-saving, highly sensitive and rapidly responding, the method also has low detection limits, with easily prepared, highly mechanically stable and reproducible modified electrodes.

2. Experiment

2.1. Reagents and chemicals

All chemicals were analytical-grade unless otherwise required. Monobasic sodium phosphate (NaH_2PO_4), dibasic sodium phosphate (Na_2HPO_4), sodium hydroxide (NaOH), phosphate (H_3PO_4) and liquid paraffin were obtained from Damao Chemical Reagent Co., Ltd. (Tianjing, China) or Guangzhou Chemical Reagent Co., Ltd. (Guangzhou, China). Fe_2O_3 nano-dispersion was received from Maylai Nami materials Co., Ltd. (Guangzhou, China). Triton X-100 was obtained from Farco International Co., Ltd. (Hong Kong, China). Graphite, Or G and Or II were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solutions (PBS) with pH ranging from 5.5 to 8.0 were prepared by mixing stock solutions of 0.2 M NaH_2PO_4 and 0.2 M Na_2HPO_4 with H_3PO_4 (1.0 M) and NaOH (1.0 M) to the desired pH. Or G and Or II standard solutions (1.0×10^{-3} M) were prepared in deionized water daily.

Multi-walled carbon nanotubes (MWCNTs) with 95% purity (10-20 nm diameter and 10-30 μm length) were obtained from DKnano Co., Ltd. (Beijing, China), and were treated with a mixture of concentrated H_2SO_4 and HNO_3 (3:1 V/V) as reported by Thomas et al. [20] to enhance the catalytic effect.

2.2. Instrumental conditions

All the electrochemical measurements were performed on a CHI 850 C electrochemical workstation (CH Instrument, Shanghai, China). A conventional three-electrode system was used for all electrochemical experiments. Bare or modified CPE (Φ=3 mm) acted as the working electrode, and an Ag/AgCl-saturated KCl electrode and a platinum electrode were used as the reference and auxiliary electrodes (Gaoss Union, Wuhan, China), respectively. All the electrochemical measurements were operated in N_2-saturated 0.1 M PBS (pH 7.0). X-ray diffraction (XRD) was performed with an Empyrean diffractometer (PANalytical, Holland) in the grazing incidence mode with a scintillator detector using Cu-Kα radiation.

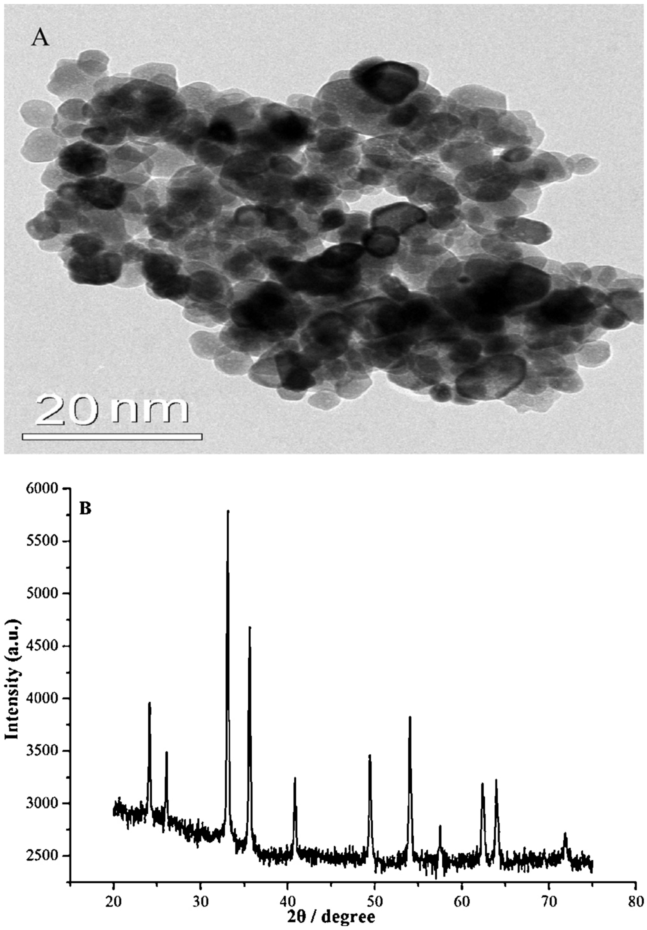

Fig. 1. TEM image of **(A)** Fe_2O_3/MWCNTs-COOH and **(B)** XRD pattern of the Fe_2O_3/MWCNTs-COOH.

Transmission electron microscopy (TEM) image was obtained from a JEM-2010HR microscope (JEOL, Japan) at an accelerating voltage of 200 kV.

2.3. Preparation of Fe_2O_3/MWCNTs-COOH/OP modified electrode

Ionic liquid-modified CPE was fabricated by the following procedure as reported by Gao et al. [21]. Initially, graphite powders

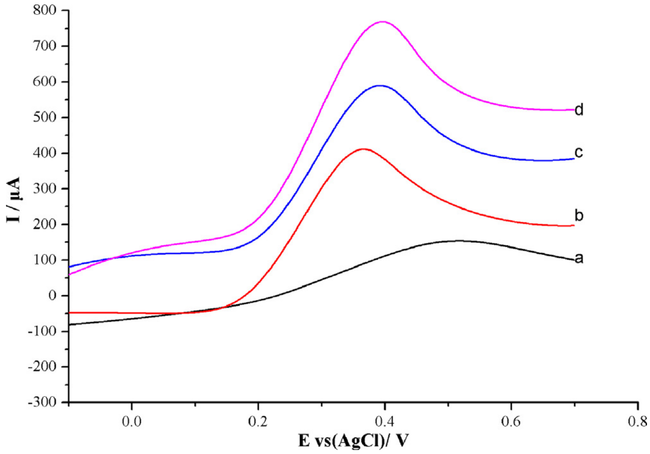

Fig. 2. LSV of 5.0 mM $K_3Fe(CN)_6$ containing 0.1 M KCl at (a) bare CPE, (b) pMWCNTs-COOH/CPE, (c) cMWCNTs-COOH/OP/CPE and (d) Fe_2O_3/MWCNTs-COOH/OP/CPE. Scan rate: 0.1 V s^{-1}.