Analytica Chimica Acta 779 (2013) 22–34

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

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

Fabrication of β-cyclodextrin-coated poly (diallyldimethylammonium chloride)-functionalized graphene composite film modified glassy carbon-rotating disk electrode and its application for simultaneous electrochemical determination colorants of sunset yellow and tartrazine

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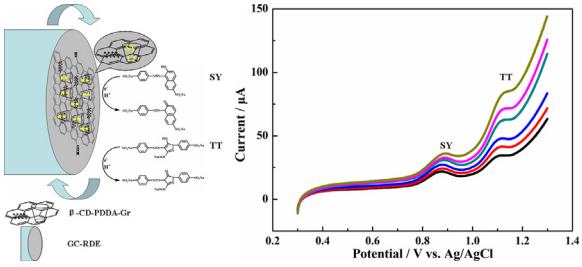
HIGHLIGHTS

- A green and facile approach for synthesis of β-CD-PDDA-Gr at room temperature.
- We present the β-CD-PDDA-Gr modified GC-RDE for simultaneous detection of SY and TT.
- SY and TT's electrooxidations are both the one-electron-one-proton-transfer process.
- Diffusion coefficients and standard rate constants of SY and TT were discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 January 2013
Received in revised form 20 March 2013
Accepted 25 March 2013
Available online 6 April 2013

Keywords:
Glassy carbon-rotating disk electrode
Kinetic parameters
Functionalized graphene
Simultaneous determination
Sunset yellow
Tartrazine

ABSTRACT

We proposed a green and facile approach for the synthesis of β-cyclodextrin-coated poly(diallyldimethylammonium chloride)-functionalized graphene composite film (β-CD-PDDA-Gr) by using L-ascorbic acid (L-AA) as the reducing agent at room temperature. The β-CD-PDDA-Gr composite film modified glassy carbon-rotating disk electrode (GC-RDE) was then developed for the sensitive simultaneous determination of two synthetic food colorants: sunset yellow (SY) and tartrazine (TT). By cyclic voltammetry (CV), the peak currents of SY and TT increased obviously on the developed electrochemical sensor. The kinetic parameters, such as diffusion coefficient D and standard heterogeneous rate constant k_b, were estimated by linear sweep voltammetry (LSV). Under the optimal conditions, the differential pulse voltammetry (DPV) signals of SY and TT on the β-CD-PDDA-Gr modified GC-RDE were significantly enhanced. The enhanced anodic peak currents represented the excellent analytical performance of simultaneous detection of SY and TT in the range of 5.0×10^{-8} to 2.0×10^{-5} mol L^{-1}, with a low limit of detection (LOD) of 1.25×10^{-8} mol L^{-1} for SY and 1.43×10^{-8} mol L^{-1} for TT ($S N^{-1} = 3$). This proposed method displayed outstanding selectivity, good stability and acceptable repeatability and reproducibility, and also has been used to simultaneously determine SY and TT in some commercial soft drinks with satisfactory results. The obtained results were compared to HPLC of analysis for those two colorants and no significant differences were found. By the treatment of the experimental data, the electrochemical reaction mechanisms of SY and TT both involved a one-electron-one-proton-transfer process.

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http://dx.doi.org/10.1016/j.aca.2013.03.061

1. Introduction

Synthetic colorants, a very important class of food additives, are usually added to food products, such as fruit juice beverages, carbonated drinks, candy, to improve appearance, color and texture [1]. Generally, the presence and content of these substances, which contain azo (N=N) functional groups and aromatic ring structures, must be controlled strictly by laws because of their potential risks to human health [2]. Sunset yellow (SY) and tartrazine (TT) are two of these azo colorants (seen Scheme 2) which will lead to the appearance of allergies, asthma, eczema, anxiety, migraines and even induce the development of cancer and other diseases [3]. The acceptable daily intake (ADI) of SY and TT given by FAO/WHO in 1994 are 2.5 mg kg^{-1} and 0.75 mg kg^{-1}, respectively. In China, the maximum amounts of the authorized synthetic dyes in SY and TT vary according to the nature of the dye. For SY and TT, they are both usually ranging from 0 to 100 mg g^{-1}, but numerous commercial products are not in accordance, the dyes contents exceeding the allowed quantities. However, several countries (European University Association and some European countries) have already banned some of these colorants such as SY which is considered carcinogenic in some countries like Finland and Norway. Therefore, it appears extremely urgent to identify and quantify with accuracy the dyes SY and TT present in food products.

Until now, literature reports showed that SY and TT have been analyzed, individually or simultaneously, using a wide range of techniques, such as spectrophotometry [4], high performance liquid chromatography–mass spectrometry (HPLC–MS) [5], fluorescence emission spectrometry [6], capillary electrophoresis [7]. Nevertheless, some of these methods and techniques are expensive, time-consuming, or required complicated pretreatment, which restrict their further applications. Compared with these methods, electrochemical methods are supposed to be a good choice due to their low cost, simplicity, good stability, and high sensitivity. In recent years, the electrochemical determination of SY or TT has been proposed utilizing different techniques based on various chemically modified electrodes [8–15]. Additionally, in this work here, the electrochemical reaction mechanisms of both SY and TT were discussed including the estimation of the diffusion coefficients and the standard heterogeneous rate constants. Furthermore, for all we know, the modification on GC-RDE with β-CD-PDDA-Gr to achieve facile and precise determination of SY and TT simultaneously remains a challenge.

Graphene (Gr), a single layer of sp^2-hybridized carbon atoms in a closely packed honeycomb two-dimensional lattice, has attracted enormous attentions since its discovery in 2004 [16]. Due to the unique properties such as good mechanical strength, large specific surface area, and high conductivity, Gr has performed potential applications in nanocomposite materials [17,18], capacitors [19], nanoelectronic devices [20], transparent conductors [21], and sensors [22,23]. However, one severe problem that may hinder the further development of Gr is the re-aggregation of the graphene nanosheets in water during the reduction procedure. The poor solubility of Gr is mainly caused by the attraction van der Waals forces between Gr sheets and strong π–π stacking [19,24]. To avoid this, great efforts have been made to functionalize Gr via chemical modification with dispersive reagents, such as surfactant [25] and cyclodextrin [26].

PDDA, a linear positively charged polyelectrolyte, has been discovered as a dispersive reagent for preventing Gr sheets from agglomerated. Liu et al. demonstrated that the positively charged PDDA might be used to noncovalently functionalize Gr sheets and the PDDA-Gr displayed good conductivity, solubility and biocompatibility [27]. Thus, functionalizing Gr sheets with PDDA should be an effect strategy to increase the solubility in water. Meanwhile, cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven or eight glucose units named α-, β-, and γ-CD, which are all commercially available. Many researchers have raised great interests in CDs because of its advantages of low cost and environmentally friendly. In comparison, β-CD, a molecule comprising two rims of hydroxyl groups, could interact with various organic, inorganic and biological guest molecules into its cavities to form stable host–guest inclusion complexes without structural changes [28,29]. Therefore, the combination of β-CD and PDDA-Gr simultaneously might possess both properties of PDDA-Gr (large specific surface area, excellent conductivity, good solubility and high stability) and β-CD (high supramolecular recognition and enrichment capability), which will provide potential applications as biosensors, electronics, etc. [30,31]. Accordingly, functionalizing Gr with PDDA and β-CD could be an effective method for the extending application in analysis determination.

Many groups have employed the conventional reductants for the chemical reduction of graphite oxide (GO), such as hydrazine [24] or hydrazine derivatives [32], which are highly poisonous and extremely harmful. In contrast, L-ascorbic acid (L-AA), a nontoxic and mild reductant, has also been introduced as reductant in some reports [33,34]. During the reduction of GO, Zhang et al. stated that many reactive oxygen groups could be reduced by L-AA, and the oxidized products were soluble in water and were easy to be removed [34]. Hence, L-AA was selected as an ideal reducing agent for the synthesis of β-CD-PDDA-Gr at room temperature. By the way, the introduction of the functionalized graphene electrode could extend the effective areas of the GC-RDE, which would increase concentration of the analyses. The graphene electrode is a better electrode than some metal electrodes in amplifying the electrochemical signals, and carbonaceous material modified electrodes do less harm to human beings. Besides, RDE is one of the important tools for estimating electrochemical kinetic parameters of more complicated reaction procedures. Meanwhile, the papers of the modified RDE for the food additives determination were rarely seen [35]. Furthermore, compared to the common glassy carbon electrode (GCE), GC-RDE could amplify the reaction signals for determination and should be a good tool for monitoring the electrode reaction procedure.

In this present work, we proposed a green and facile approach for water-phase synthesis of β-CD-PDDA-Gr reduced by L-AA at room temperature. Next, a highly sensitive, simple and stable electrochemical sensor based on β-CD-PDDA-Gr was established for simultaneous determination of SY and TT on GC-RDE. More significantly, the electrode reaction mechanisms of SY and TT were both studied and some kinetic parameters of them were also calculated. These obtained results suggested that the β-CD-PDDA-Gr modified GC-RDE could be considered as an important sensor to discuss the reaction mechanism and analyze the dynamics of azo colorants. Meanwhile, the proposed methods was validated according to the International Conference on Harmonization (ICH) guidelines and successfully applied for determination of SY and TT in pure form and in drinks samples with satisfactory results.

2. Experimental

2.1. Apparatus and reagents

Graphite flake (natural, −325 mesh, 99.8%) was purchased from Alfa Aesar. Nafion-117 (5 wt.%) and PDDA (20 wt.% in water) with a molecular weight from 100,000 to 200,000 were from Aldrich reagent company and used directly. β-CD and L-AA were obtained from Sigma. The ultra-pure water was prepared by the Milli-Q system (Milli-pore Inc., nominal resistively 18.2 MΩ cm). The