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Electrochemically reduced graphene oxide-modified screen-printed carbon electrodes for a simple and highly sensitive electrochemical detection of synthetic colorants in beverages

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ABSTRACT

A simple and highly sensitive electrochemical sensor based on an electrochemically reduced graphene oxide-modified screen-printed carbon electrode (ERGO-SPCE) for the simultaneous determination of sunset yellow (SY) and tartrazine (TZ) was proposed. An ERGO film was coated onto the electrode surface using a cyclic voltammetric method and then characterized by scanning electron microscopy (SEM). In 0.1 M phosphate buffer at a pH of 6, the two oxidation peaks of SY and TZ appeared separately at 0.41 and 0.70 V, respectively. Surprisingly, the electrochemical response remarkably increased approximately 90- and 20-fold for SY and TZ, respectively, using the modified electrode in comparison to the unmodified electrode. The calibration curves exhibited linear ranges from 0.01 to 20.0 μM for SY and from 0.02 to 20.0 μM for TZ. The limits of detection were found to be 0.50 and 4.50 nM (at S/N=3) for SY and TZ, respectively. Furthermore, this detection platform provided very high selectivity for the measurement of both colorants. This electrochemical sensor was successfully applied to determine the amount of SY and TZ in commercial beverages. Comparison of the results obtained from this proposed method to those obtained by an in-house standard technique proved that this developed method has good agreement in terms of accuracy for practical applications. This sensor offers an inexpensive, rapid and sensitive determination. The proposed system is therefore suitable for routine analysis and should be an alternative method for the analysis of food colorants.

1. Introduction

With the beginning of a new era in the food industry, more food additives have been introduced to aid in food preservation and processing. The use of food additives has also been proven to extend the shelf-life and/or enhance the food quality and texture [1]. However, these food additives can only be incorporated in certain food products, and they must fall within a specified dosage as well as have a justified purpose. A food additive overdose is considered as food adulteration, as these foods possess toxicity or lack any technical-functional purpose. Therefore, the use of food additives in the food industry requires ethical consideration [2].

Food colorants, either synthetic or in a natural form, are normally used as food additives to enhance consumer acceptance. Sunset yellow (SY, E110) and tartrazine (TZ, E102), classified as azo dyes, are common synthetic colorants that are extensively employed in the food industry due to their low production cost, charming color uniformity and excellent water solubility as well as their high stability to light, oxygen and pH [3–5]. However, they can cause detrimental effects to health when they are excessively consumed. In recent studies, extensive consumption of SY and TZ was found to significantly decrease the thymus weight and alter the monocyte counts as well as induce allergic responses including contact urticaria, angioneurotic edema, asthma, contact anaphylaxis and immunosuppression in humans [6,7]. Because they are harmful to human health, the use of colorants as food additives is strictly controlled by laws and regulations. The maximum acceptable content by the international and national legislation is 100 μg/mL when they are employed individually or in

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combination [8]. The European University Association and some European countries such as Finland and Norway have already excluded these colorants and consider them to be carcinogenic agents [9]. According to Thai Food Act B. E. 2547, notification 281, colorants are not permitted to be incorporated into many food categories such as pickled/osmosed fruit, fresh-cut fruit, processed meat, smoked meat and dried meat. Yet, some manufacturers illegally incorporate these substances into their products. The presence of colorants in food samples indicates that some food producers lack responsibility and ethics, and it also indicates that these colorants are still widely used in foods beyond the use permitted by rules and regulations [10].

Various techniques have been developed and applied over the last few decades for the examination of SY and TZ. Currently, the most widely used techniques for the determination of colorants are spectrophotometry [11], high performance liquid chromatography (HPLC) [12], column chromatography [13], and capillary electrophoresis [14]. Nevertheless, the first two aforementioned techniques have some disadvantages. In particular, these two techniques exhibit low sensitivity and specificity, require expertize, are time-consuming, and require instrumentation that is complicated as well as expensive. Therefore, a detection method that offers a short analysis time, a simple and low cost process, high sensitivity and high selectivity is still in demand and important for food safety and human health.

Different electrochemical methods for the simultaneous determination of SY and TZ in commercial beverages have been reported. The high sensitivity, small sample volume requirement, low cost, simplicity, short analysis time and portability are the key requirements of a detection method. Various types of electrodes have been employed to successfully fabricate a sensor that allowed simultaneous measurement of SY and TZ. Examples of such electrodes include a pretreated boron-doped diamond electrode, a graphene phosphotungstic-modified glassy carbon electrode (GN-PTA/GCE), a graphene TiO_2-modified GCE (GN-TiO_2/GCE), a gold nanoparticle-modified carbon paste electrode (Au NPs/CPE), a multi-walled carbon nanotubes-modified GCE (MWCNT/GCE) and a platinum wire-coated electrode [15–20]. Unfortunately, these electrodes are non-disposable and rather expensive to use for the routine analysis of food colorants. Therefore, a critical step towards routine analysis is the development of a disposable sensor that simultaneously detects SY and TZ without compromising the electrochemical sensitivity and selectivity.

Graphene, a single sheet of carbon atoms settled in a honeycomb lattice, has recently received research interest due to its potential in improving the conductivity of the modified sensor. It has been applied in many applications, especially in the electrochemical field. Graphene-modified electrochemical sensors have been reported in the detection of phytohormones, biomolecules, pharmaceuticals, food additives and environmental pollutants [21–25]. However, it was found that graphene tends to form irreversible agglomerates through strong π-π stacking and Van der Waals interactions, which restricts its application and storage [26].

Chemically synthesized graphene has been considered to be a new substitute for graphene because of its similar characteristics and ease of synthesis. Synthetic graphene is usually obtained from reduced graphite oxide prepared via Hummers's method, followed by reducing the ultrasonically exfoliated graphene oxide (GO) with hydrazine [27]. An alternative method reported for the preparation of graphene involves reacting sodium metal and ethanol, followed by thermal exfoliation and reduction of the GO intermediate [28]. Although a simpler method for graphene synthesis has been reported, preparation of a graphene solution for further electrode modification is troublesome. Recently, the GO intermediate has received intense research interest due to its convenience in storage and fast dissolution in water without any dispersing agents. However, among these reduction methods, both chemical and physical reduction of an intermediate still possess some disadvantages because of the toxicity of reducing agents, expense and several steps in the reduction process.

Recently, an environmentally friendly electrochemical reduction of GO with controllable size and thickness has been reported. This technique is an attractive alternative method for the reduction of GO to obtain a graphene sheet due to its simple instrumental setup. Moreover, it also offers easy preparation, cost-effectiveness and non-toxicity. The electrochemical reduction of GO film (ERGO) obtained by employing this technique can enhance the large specific surface area and electrochemical conductance of the electrochemical sensor, thus improving the analytical performance [29].

An electrochemical sensor for the simultaneous determination of SY and TZ using an electrochemically reduced graphene oxide-modified screen-printed carbon electrode (ERGO-SPCE) has not yet been reported. Therefore, the main objective of this work is to propose a simple and highly sensitive electrochemical sensor based on an ERGO-SPCE to use as a novel method for the determination of SY and TZ. A green and facile routine electrochemical reduction method was employed to produce an ERGO film onto the electrode surface in one step. This disposable SPCE employed was inexpensively and easily prepared. Analytical parameters, such as the sensitivity, selectivity and reproducibility, were also investigated. This developed electrochemical sensor was also applied to quantify the amounts of SY and TZ in practical samples to validate the performance of the developed sensor.

2. Experimental

2.1. Chemicals and apparatus

Graphite powder (mesh size $< 100\ \mu m$) was purchased from Sigma Aldrich (CA, USA). Carbon ink and silver/silver chloride were purchased from Acheson (CA, USA). The screen-printed block was made by Chaiyaboon Co. Ltd. (Bangkok, Thailand). Analytical grade diethylene glycol monobutyl ether and ethylene glycol monobutyl ether acetate, as binder solution in the ink preparation step, and other analytical grade reagents were purchased from Merck (CA, USA). Food grade, sunset yellow (batch: 21,023) and tartrazine (batch: 20,633) standard samples were obtained from BRENNTAG Co. Ltd. (Bangkok, Thailand). Graphene oxide (GO) was purchased from XF Nano, Inc. (Nanjing, China).

All electrochemical measurements were performed on a PGSTAT 30 potentiostat (Metrohm Siam Co. Ltd.) and controlled with the general purpose electrochemical system (GPES) software (Utrecht, Netherlands). A disposable screen-printed carbon electrode (SPCE) was fabricated using an in-house screen-printing method. All measurements were conducted using a differential pulse voltammetric method at room temperature (25 °C). The surface morphologies of the unmodified and modified electrode were verified using scanning electron microscopy (SEM). The presence of the ERGO film on the electrode surface was monitored employing infrared spectroscopy (IR).

For the analysis employing compendium of method, used in parallel with the proposed approach to confirm the accuracy and acceptability of method, the system consisted of a pump (Model CM 3200), UV–vis detector (absorbance at 235 nM, model SM 3200), C18 column (250 mm × 4.6 mm i.d.; particle size, 5 μm, Phenomenex). The separation was carried out with an isocratic elution consisting of 5 mM tetra-*n*-butyl ammonium hydroxide (TBAH), pH 4.5:ACN (52:48v/v) with an injection volume of 20 μL, flow rate of 1.2 mL min^{-1}.