TRANSACTIONS ON SCIENCE AND TECHNOLOGY

Sensitive Determination of Tartrazine (E 102) Based on Chitosan/Nanoparticles/MWCNTs Modified Gold Electrode in Food and Beverage Products

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Received: *20 March 2016*
Revised: *5 April 2016*
Accepted: *23 April 2016*
In press: *24 April 2016*
Online: *30 June 2016*

Abstract

Food dyes can be categorized into natural and synthetic color. Tartrazine (E 102) which belong to the family of azo dyes and commonly used in food industry. Tartrazine imparts positive and negative benefits as well, by giving attractive physical appearance and consumer acceptance for over centuries. However, excessively intake of food Tartrazine can cause toxicity and pathogenicity to human. Due to arising of the health issues to mankind, researchers gave attentions for determination of Tartrazine by using analytical and advance methods. Currently, there are several analytical methods available, however, these methods are required skilled persons, time consuming and high cost. Herein, an electrochemical sensor was developed based on the combination of nanomaterials (chitosan, calcium nanoparticles and multiwall carbon nanotubes) for detection of Tartrazine. Electrochemical behavior of the modified gold electrode in the presence of Tartrazine was studied by using cyclic voltammetry and differential pulse voltammetry. Under optimal conditions, the DPV was detected with different concentrations of Tartrazine in the range of 0.1 to 10 ppm, with low detection limit (3.3σ/s).

Keywords:
Tartrazine; Chitosan; multiwall carbon nanotubes; nanoparticles; electrochemical sensor

Introduction

Color is an important attribute when it comes to food choices. Food colorants are added to the food to enhance its appeal and acceptability. Soluble food dyes are classified as three main groups that are natural food dye, nature-identical food dye, and synthetic food dye. Natural food dye is compound originating from plant sources such as anthocyanins, betalain, chlorophylls, carotenes, and curcumin. However, natural dye is unstable and can be characterized by their own physiological activity. Nature-identical food dye is food coloring compound synthesized to the chemical identity of the natural food dye. Synthetic food dye is stable and has more permanent color compare to natural and nature-identical food dyes. Synthetic food dye is a product of chemical process in which molecules which are

capable of imparting colors to food are synthesized. Azo dyes, chinilin, xanthan, and antrachinon dyes are the main classes of synthetic food dyes (Khanavi *et al.*, 2012; Amchova *et al.*, 2015).

Tartrazine (E 102) is an azo group food dye, orange-colored, water-soluble powder commonly used in food products, drugs, cosmetics, and pharmaceuticals. It is also known as Food Drug & Cosmetic (FD&C) Yellow No. 5, C.I. No. 19140, Food Yellow No. 4 with code number E 102. Tartrazine is primarily the 3-carboxy-5-hydroxy-1-(4'-sulfonatophenyl)-4-(4'-sulfonatophenylazo)-H-pyrazol-3-carboxylate. High concentration of Tartrazine in food may be harmful and in a small portion of population, even a small dose can give rise to health complication such as hyperactivities in children when combined with sodium benzoate. The Acceptable Daily Intake (ADI) of Tartrazine was set at 0-7.5 mg/kg bw/day by Joint FAO/WHO Expert Committee on Food Additive (JECFA) and EU Scientific Committee for Food (SCF). The maximum level of Tartrazine in non-alcoholic beverages should not be more than 0.01 g/mL, and manufacturers should follow the regulation (De Andrade *et al.*, 2014).

In this study, a novel electrochemical sensor was developed based on chitosan, calcium nanoparticles and multiwall carbon nanotubes modified gold electrode (CHIT/CaONPs/MWCNTs/AuE) for the determination of Tartrazine in foodstuffs. The CaONPs offer a synergistic electrocatalytic effect toward Tartrazine including large specific surface area of MWCNTs. Electrochemical behavior of the modified gold electrode in the presence of Tartrazine was studied by using cyclic voltammetry and differential pulse voltammetry. The schematic mechanism oxidation of Tartrazine took place a one-electron and one-proton irreversible reaction on CHIT/CaONPs/MWCNTs/AuE shown in Figure 1. The fabricated Tartrazine sensor reveals a wide linear range from 0.1 to 10 ppm, with low detection limit, high selectivity, and long-term stability. It is expected that this new method will have broad applications in determination of biological substances and food colorants.

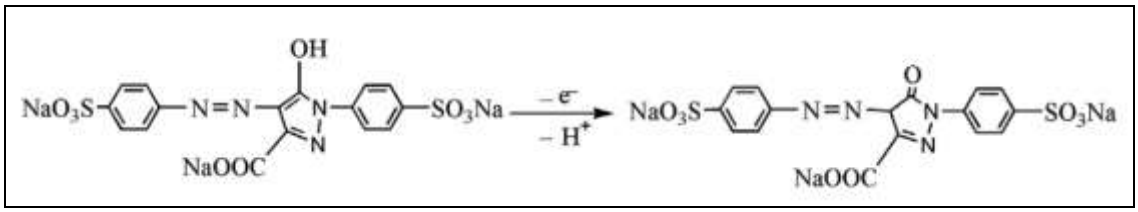

Figure 1. Oxidation mechanism for the electrochemical process of Tartrazine (Qiu *et al.*, 2016)

Methodology

Chemical and reagents

Tartrazine (E 102), Chitosan (CHIT) and multiwall carbon nanotubes (MWCNTs) were purchased from Sigma Aldrich (USA). Calcium oxide nanoparticles (CaONPs) were obtained from Biosensors and Bioelectronics Laboratory, Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. Tartrazine (50 ppm) was dissolved into dH_2O as a stock solution and stored at 4°C. Other

chemicals were of analytical reagent grade and used as received. All solutions were prepared using deionized water as the solvents and were carried out at room temperature condition of 25 ± 0.1°C.

Apparatus and equipment

All electrochemical measurements were carried out with a µ-autolab (Ecochemie, The Netherlands) voltammetric analyzer using the software package on NOVA 1.8 for CV and DPV analysis. A three-electrode systems were used in the measurement which composed of a gold electrode (d=3 mm) as working electrode, Ag|AgCl|KCl as the reference electrode and the platinum wire as counter electrode.

Preparation and immobilization of CHIT/NPs/MWCNTs

The gold electrode (AuE) was pre-treatment by polished with 3 µM aluminum slurry for 2 min and sonicated for 2 min. Then, the AuE was rinsed with deionized water about 2 min. For modification of AuE, CHIT solution was prepared by dissolving the CHIT powder in acetic acid. The solution was stirred for at least 4 h at room temperature until the CHIT was fully dissolved. CaONPs were added into the CHIT solution was then sonicated for 20 min. It was stirred for 8 h for highly dispersed colloidal suspension. Again 1 % of MWCNTs was added in the CHIT/CaONPs mixture and sonicated to produce a homogenous suspension. After that, MWCNTs mixtures were allowed the formation of a uniform CHIT/CaONPs/MWCNTs nanocomposite suspension (Kobun *et al*., 2015a; Kobun *et al*., 2015b).

Extraction of real samples

Candy, jelly and soft drink were selected as detection samples in this work previously reported by Sahraei *et al.* (2013). The samples were purchased from the local super market in Kota Kinabalu, Sabah, Malaysia. Firstly, candy and royal jelly were respectively dissolved in 100 mL hot pure water (~45°C). Each of the samples was filtered through a 0.45 µm membrane filter to obtain solution without precipitation for subsequent use (Shawish *et al*., 2013). The soft drink sample was used directly without any pretreatment. Finally, sample extract was added into working buffer, and then analyzed according to the optimization electrochemical sensor protocols.

Result and discussion

Detection of Tartrazine

The detection limit of developed sensor was determine using Differential pulse voltammetry (DPV) technique. Figure 2 shows the DPV responses with different concentrations of Tartrazine in supporting electrolyte. Under optimum conditions, the developed sensor was detected Tartazine in the range of 10-1 ppm, with detection limit of 0.9 ppm. At potential volt -0.18, a linear regression equation was expressed as I (10^{-6} A) = 4.6947 (ppm) + 15.432, with correlation value of r^2 = 0.99354.

These results indicated a very good analytical performance of the developed electrochemical sensor in real samples analysis.

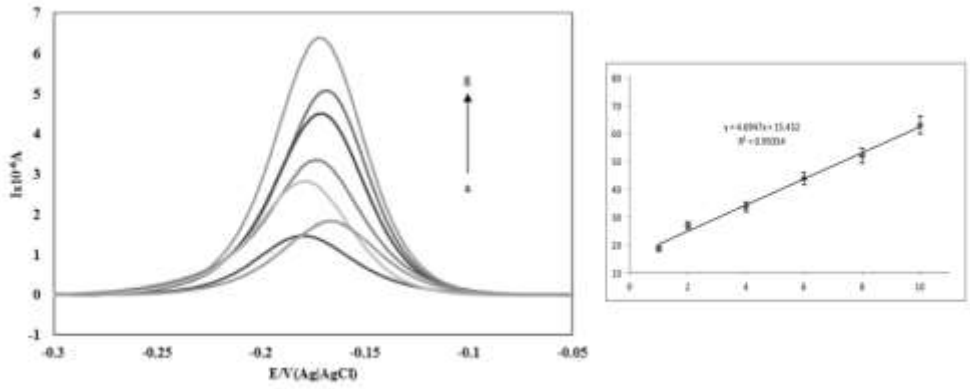

Figure 2. DPV method was measured with different concentrations of Tartrazine at pH 7.0 supporting electrolyte (a-g: 0, 1, 2, 4, 6, 8, and 10 ppm). Inset: calibration plots of the oxidation peak currents as a function of Tartrazine.

Analysis of real samples

The developed sensor was successfully applied for determination of Tartrazine in some food and beverage samples bought from local market at Kota Kinabalu, Malaysia. There are three different samples were analyzed including candy, jelly and soft drink. The samples were extracted and spiked with different concentration of Tartrazine standard. The accuracy of the developed sensor was analyzed by performing and calculate the recovery rate. Based on the result summarize in Table 1, the recovery rate was calculated to be 93.2 to 96.6%, showing good accuracy and feasible. Each sample was conducted three times, and the relative standard deviation (RSD) was found lower than 1%, revealing that the results obtained are acceptable and good precision. Hence, the developed method able to applied for detection of Tartrazine in food and beverage products.

Table 1. Recovery studies of food products.

Samples	Recovery	RSD (%)
Candy	96.6	0.18
Jelly/gelatin	93.2	0.37
Soft drink (liquid)	95.1	0.21

Conclusion

A simple and rapid electrochemical sensor has developed based on CHIT/CaONPs/MWCNTs modified gold electrode. The developed method exhibited high sensitivity and stability for the detection of Tartrazine. The peak currents increased with the increasing Tartrazine concentration from 10 to 1 ppm. The detection limit calculated is 0.9 ppm, which is lower than traditional methods, with

linear coefficient of 0.99354 and the recovery rate of food beverages products are 93.2 to 96.6%. The developed method is successfully applied for determination of Tartrazine level in food products. The developed electrochemical sensor offers a simple, fast, high selectivity and sensitivity, wide detection range and convenient method for use in food research laboratories.

Acknowledgements

This work was supported by grants from the Ministry of Education Malaysia, Fundamental Research Grant Scheme (FRGS) (No. FRGS/1/2014/SG05/UMS/02/4).

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