Selective Electrochemical Sensor for the Determination of Tartrazine in Food Products

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ABSTRACT A novel electrochemical sensor based on modified glassy carbon electrode with chitosan, gold nanoparticles, multi-walled carbon nanotubes and graphene oxide (CHIT/AuNPs/MWCNTs/GO) was developed for sensitive quantification of Tartrazine (TZ) in food products. The morphological characteristics of CHIT/AuNPs/MWCNTs/GO were investigated by scanning electron microscopy (SEM) and electrochemical tests. Under optimal condition, DPV results presented high stability and excellent electrocatalytic activity of CHIT/AuNPs/MWCNTs/GO for the determination of TZ level and wide concentration ranges with linear regression was y=0.054x-0.2511 (r^2=0.99037). Also, the developed sensor was successfully applied jelly, candy as well as soft drinks which showed good selectivity with satisfactory results. The developed sensor offers faster detection and low cost which can be an alternative technique in monitoring synthetic food colorants.

KEYWORDS: Food colorant, Tartrazine, electrochemical detection, chitosan, gold nanoparticles, multi-walled carbon nanotubes, graphene oxide

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INTRODUCTION

Synthetic colorants are commonly used in a variety of foods products due to low manufacture cost, less microbiological pollution, good water solubility, high stability to oxygen, light and pH changes (Wu et al., 2018). Tartrazine (TZ) is bright yellow azo synthetic colorants that typically added ingredient found in foods, drinks, medications, toiletries, supplements, cosmetics products, and other non-nourishment stuff (Wang and Zhao, 2015). At the international level, there is an indicator evaluated and revealed by the Joint FAO/WHO Committee on Food Additives (JECFA) known as acceptable daily intake (ADI) (JECFA, 2014). However, high consumption of TZ may cause severe side effects including allergic responses, asthma, reproductive toxicity, cancer, DNA damage and thyroid cancer (Majidi et al., 2014). Thus, due to the controversial issues, there is needed for precise and straightforward analytical techniques to monitor and quantify the level of TZ in food products.

There are several methods have been developed for the determination of TZ including HPLC (Ma et al., 2006), stopped-flow analysis (Schenone et al., 2013), spectrophotometry method (Sahraei et al., 2013) and fluorescence method (Xu et al., 2015). However, those techniques have limitations in terms of the sample preparation procedures, time-consuming and expensive in terms of instruments practice (Molaakbari et al., 2014). Hence, electrochemical is one of the alternative methods which owing to its low-cost analytic tools, simple procedure, long-term stability, high sensitivity and selectivity in sensing of analytes (Wang et al., 2014). Recently, innovative materials such as carbon nanomaterials and metal nanoparticles have been discovered with unique properties for numerous applications.

Graphite, known as honeycomb lattice which rich of single-atom-thick layer carbon that has a large specific surface area, and stable in electrochemical proses (Chen et al., 2012). Graphene oxide (GO) found high interest in biosensing field because of sizeable available surface area, simple

procedure synthesis, excellent water dispersibility, and biocompatibility, (Song et al., 2016). Gold nanoparticles are one of the popular nanoparticles used in biosensor field due to high adsorption ability, good electron transfer, and stability, as well as surface reactivity (Rovina et al., 2016; Wang et al., 2015). By combining the above characteristics, CHIT/AuNPs/MWCNTs/GO modified electrode was developed for sensitive determination of the TZ in the food products.

METHODOLOGY

Reagents

Tartrazine, graphite, multi-walled carbon nanotubes and chitosan were bought from Sigma-Aldrich (USA). Phosphate buffer solution (PBS) acts as supporting electrolyte. All chemicals were of analytical grade and prepared using doubly distilled water without any additional purifications.

Instruments

Scanning Electron Microscopy (SEM) was accomplished by using S-3400N Hitachi (Japan). The voltammetry analysis was performed using Multi Potentiostat/Galvanostat μStat 8000 electrochemical analyzer controlled by DropView Software. There are the three-electrode system used which are glassy carbon electrode (GCE) as a working electrode, Ag|AgCl electrode as a reference electrode and a platinum electrode used as the auxiliary electrode. All measurements were performed at room temperature.

Preparation of nanomaterials (GO/AuNPs)

Graphene oxide (GO) was prepared by following Hummers and Offemans (1958) method with slight modification. 10 mg natural graphite powder GO, and 0.06 g potassium permanganate ($KMnO_4$) was dispersed and sonicated in 20 mL double distilled water for 1h at room temperature. H_2SO_4: H_3PO_4 (1:10) was added to the mixture and continuously stirred at 50 ^{o} for 12 h. Finally, the mixture was centrifuged and washed successively with HCl, ethanol, and ether until in natural condition. The final product of GO was dried overnight and stored for further used.

AuNPs were prepared by the citrate reduction technique as formerly designated by Grabar et al. (1995). All glassware's were immersed in aqua regia (HNO3/HCL, ratio 1:3) solution and rinsed thoroughly with double distilled water. Then, 100 mL of 1 mM chloroauric acid ($HAuCl_4$) was heated on a magnetic hot plate. A 5 mL of trisodium citrate (38.3 mM) was instantly added into boiling $HAuCl_4$ solution and stirred vigorously for 15 min. The solution was stored at 4 ^{o}C for further experiment.

Fabrication of the modified electrode

Before modification, the surface of GCE was polished to a mirror-like surface with 3 μM aluminum slurry on a micro cloth pad and sonicated in mixture 70 % ethanol for 2 min (Rovina et al., 2017). Then, 5 μL of CHIT/AuNPs/MWCNTs/GO solution was dropped on the GCE surface and dried at room temperature. The successfully acquired modified electrode was represented as CHIT/AuNPs/MWCNTs/GO/GCE. The modified electrodes were stabilized by performed cyclic potential scanning from 0 V to + 2.0 V in PBS electrolyte solution for 20 cycles.

Preparation of food samples

The extraction of candies, jellies, and soft drinks was followed by Bonan et al. (2013) method. For candies and jellies, 4 g of samples and 20 mL of ethanol-water were homogenized for 15 min. The samples were then shaken for 1 h. For soft drink analysis, 4 mL of soft drink was degassed by

ultrasonic bath for 20 min and diluted with dH_2O (1:1 v/v). Finally, all samples were centrifuged (15 000 rpm) for 10 min at 0 °C. Then, the supernatant was filtrated using 0.45 μm filter membrane. All the current measurements were recorded and compared using DPV technique.

RESULT AND DISCUSSION

Morphological characterization of nanomaterials

The surface morphologies of CHIT, CHIT/MWCNTs, CHIT/GO, and CHIT/AuNPs/MWCNTs/GO were characterized by scanning electron microscope (SEM) are shown in Figure 1. Figure 1a and Figure 1b clearly show highly porous of CHIT and CHIT/MWCNTs. There are bundles of MWCNTs were interconnected to form netlike and highly porous nanostructure since the strong π-π electronic interactions and low attachment of the oxygenated groups with MWCNTs. Figure 1c of graphene oxide with CHIT (CHIT/GO) showed the minimal thickness of the nanomaterials structure. It is seen that the two carbon materials of GO and MWCNTs have particularly had distinctive morphologies. The CHIT/AuNPs/MWCNTs/GO shown the well-dispersed of AuNPs adhere well to the CHIT/GO/MWCNTs nanocomposite as displayed in Figure 1d. Overall, the structure of the CHIT/AuNPs/MWCNTs/GO was synthesized successfully.

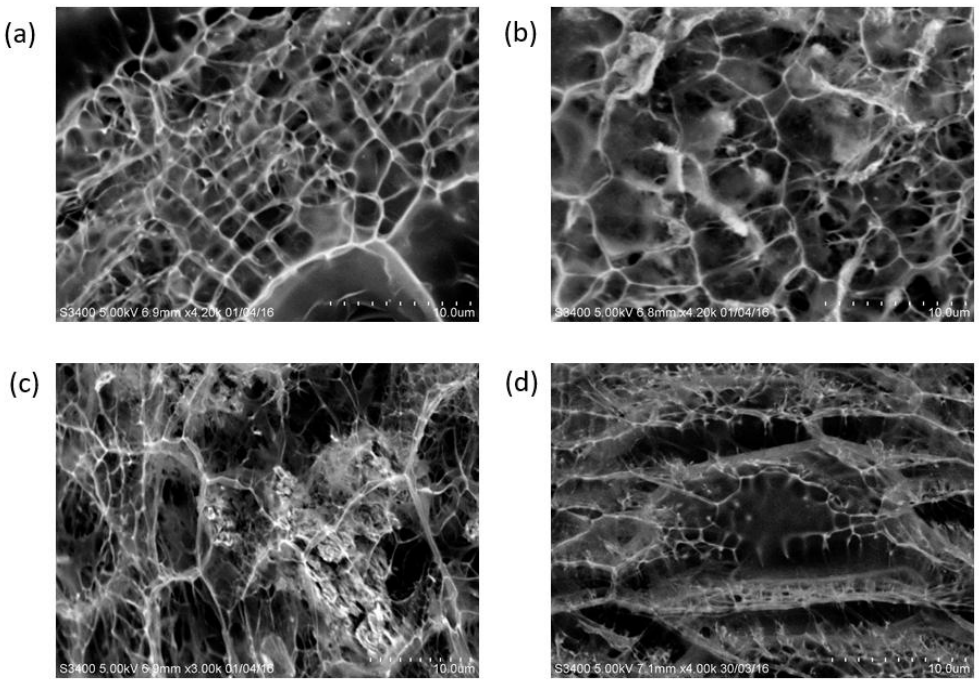

Figure 1. SEM images of the (a) CHIT, (b) CHIT/MWCNTs, (c) CHIT/GO, and (d) CHIT/AuNPs/MWCNTs/GO.

Limit of detection

Under optimum conditions, the different effect concentration of TZ towards advanced sensor was studied shown in Figure 2. The peak current for the oxidation signal of TZ was increased when the concentration increases. The oxidation current signal showed a linear in the range from 0 to 90 mg mL^{-1} with regression line (R^2) values of TZ were found to be 0.99037 mg mL^{-1}, which indicated good linearity. The modified electrode showed good accumulation efficiency and significant surface enhancement effects for the electro-oxidation of TZ due to the large surface area and high immobilization capacity. The detection limit compared with other reported works are summarized

in Table 1, and showed excellent properties of the different morphological as well as low detection limit.

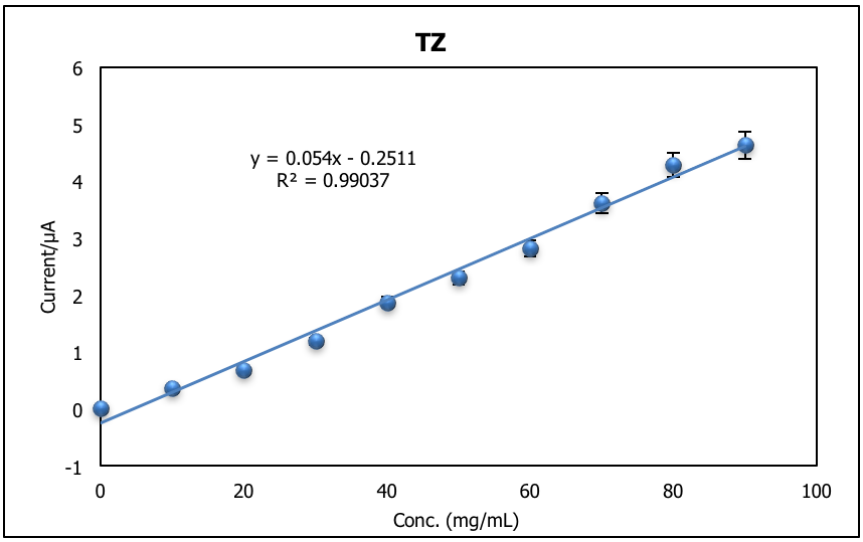

Figure 2 Calibration curve of the oxidation peak currents obtained by differential pulse voltammetry and the logarithm of TZ concentrations (I_{pc} vs log M).

Table 1 Comparison of existing electrochemical methods

Methods	Liner range	Limit of detection	References
Modified glassy carbon electrode with poly (3, 4-ethylenedioxythiophene)	0.1 - 206 μM	0.032 μM	Sakthivel et al. (2018)
Modified carbon paste electrode with poly (p-aminobenzenesulfonic acid)/zinc oxide nanoparticles	0349 - 5.44 μM	2.2034 μA/μM	Karim-Nezhad et al. (2017)
Modified glassy carbon electrode with ZnO/cysteic acid nanocomposite	0.07 - 1.86 μM	0.01 μM	Dorraji & Jalali, (2017).
Modified carbon paste electrode with Cu-BTC frameworks	1.0 - 100 nM	0.14 nM	Ji et al. (2016).
Modified glassy carbon electrode with gold nanorods decorated graphene oxide	0.03 - 6.0 μM	8.6 nM	Deng et al. (2016)
Modified glassy carbon electrode with CHIT/AuNPs/MWCNTs/GO	0 - 90 mg mL^{-1}	1.45 mg mL^{-1}	This work

Analytical application

The applicability of a CHIT/AuNPs/MWCNTs/GO was examined for determination of TZ in candies, jellies, and soft drinks sample purchased from the local supermarket at Kota Kinabalu, Sabah, Malaysia. All the real samples were extracted and further analysis by developed CHIT/AuNPs/MWCNTs/GO modified electrode. The recovery rate was analyzed to be from 94.52 – 109.0 %, and the sample was conducted three times, and the relative standard deviation (RSD) was discovered lower than 5 %, revealing an excellent precision of the developed sensor (Table 2). The developed electrochemical sensor presented good reliability and applicability for the determination of synthetic colorants in commercial food and beverage products as well as in biological systems or pharmaceutical preparations.

Table 2 Analysis of TZ in commercial products using CHIT/AuNPs/MWCNTs/GO

Samples	Spiked (mg mL^{-1})	Expected (mg mL^{-1})	CHIT/GO/MWCNTs/AuNPs/GCE	
			Found (mg mL^{-1})	Recovery (%)
Candy	0	-	7.49 ± 0.27	-
	50	57.49	56.01 ± 0.77	97.42
Jelly	0	-	4.35 ± 0.09	-
	50	54.35	56.24 ± 0.27	103.48
Soft drinks	0	-	10.73 ± 0.08	-
	50	60.73	59.36 ± 0.11	97.74

CONCLUSION

In this work, a sensitive and selectivity method, wide concentration range, good stability and efficient method of the electrochemical sensor (CHIT/AuNPs/MWCNTs/GO/GCE) has been developed and successfully tested for direct electrooxidation of TZ in food products. The developed sensor efficiently enhanced electron transfer and increase electrocatalytic activity toward TZ, based on the synergistic effect of CHIT/AuNPs/MWCNTs/GO. The developed sensor presents high potential applicability in the analysis of commercial products.

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REFERENCES

[1] Chen, D., Feng, H., & Li, J. (2012). Graphene oxide: preparation, functionalization, and electrochemical applications. *Chemical Reviews*, **112**(11), 6027-6053.

[2] Deng, K., Li, C., Li, X., & Huang, H. (2016). Simultaneous detection of sunset yellow and tartrazine using the nanohybrid of gold nanorods decorated graphene oxide. *Journal of Electroanalytical Chemistry*, **780**, 296-302.

[3] Dorraji, P. S., & Jalali, F. (2017). Electrochemical fabrication of a novel ZnO/cysteic acid nanocomposite modified electrode and its application to simultaneous determination of sunset yellow and tartrazine. *Food Chemistry*, **227**, 73-77.

[4] Grabar, K. C., Freeman, R. G., Hommer, M. B., & Natan, M. J. (1995). Preparation and characterization of Au colloid monolayers. *Analytical Chemistry*, **67**(4), 735-743.

[5] Hummers Jr, W. S., & Offeman, R. E. (1958). Preparation of graphitic oxide. *Journal of the American Chemical Society*, **80**(6), 1339-1339.

[6] JECFA (Joint FAO/WHO Committee on Food Additives). (2014). Guidelines for the simple evaluation of food additive intake. URL www.fao.org/input/download/standards/6/cxg_003e.pdf, accessed 25.12.2018.

[7] Ji, L., Cheng, Q., Wu, K., & Yang, X. (2016). Cu-BTC frameworks-based electrochemical sensing platform for rapid and simple determination of Sunset yellow and Tartrazine. *Sensors and Actuators B: Chemical*, **231**, 12-17.

[8] Karim-Nezhad, G., Khorablou, Z., Zamani, M., Dorraji, P. S., & Alamgholiloo, M. (2017). Voltammetric sensor for tartrazine determination in soft drinks using poly (p-aminobenzenesulfonic acid)/zinc oxide nanoparticles in carbon paste electrode. *Journal of Food and Drug Analysis*, **25**(2), 293-301.

[9] Ma, M., Luo, X., Chen, B., Su, S., & Yao, S. (2006). Simultaneous determination of water-soluble and fat-soluble synthetic colorants in foodstuff by high-performance liquid chromatography–diode array detection–electrospray mass spectrometry. *Journal of Chromatography A*, **1103**(1), 170-176.

[10] Majidi, M. R., Pournaghi-Azar, M. H., Baj, R. F. B., & Naseri, A. (2015). Formation of graphene nanoplatelet-like structures on carbon–ceramic electrode surface: application for simultaneous determination of sunset yellow and tartrazine in some food samples. *Ionics*, **21**(3), 863-875.

[11] Molaakbari, E., Mostafavi, A., Beitollahi, H., & Alizadeh, R. (2014). Synthesis of ZnO nanorods and their application in the construction of a nanostructure-based electrochemical sensor for determination of levodopa in the presence of carbidopa. *Analyst*, **139**(17), 4356-4364.

[12] Rovina, K., Siddiquee, S., & Shaarani, S. M. (2016, June). Highly sensitive determination of sunset yellow FCF (E110) in food products based on Chitosan/Nanoparticles/MWCNTs with modified gold electrode. In *IOP Conference Series: Earth and Environmental Science* (Vol. **36**, No. 1, p. 012023). IOP Publishing.

[13] Rovina, K., Siddiquee, S., & Shaarani, S. M. (2017). Highly sensitive electrochemical determination of sunset yellow in commercial food products based on CHIT/GO/MWCNTs/AuNPs/GCE. *Food Control*, **82**, 66-73.

[14] Sahraei, R., Farmany, A., & Mortazavi, S. S. (2013). A nanosilver-based spectrophotometry method for sensitive determination of tartrazine in food samples. *Food chemistry*, **138**(2-3), 1239-1242.

[15] Sakthivel, M., Sivakumar, M., Chen, S. M., & Pandi, K. (2018). Electrochemical synthesis of poly (3, 4-ethylenedioxythiophene) on terbium hexacyanoferrate for sensitive determination of tartrazine. *Sensors and Actuators B: Chemical*, **256**, 195-203.

[16] Schenone, A. V., Culzoni, M. J., Marsili, N. R., & Goicoechea, H. C. (2013). Determination of tartrazine in beverage samples by stopped-flow analysis and three-way multivariate calibration of non-linear kinetic-spectrophotometric data. *Food Chemistry*, **138**(2-3), 1928-1935.

[17] Song, Y., Luo, Y., Zhu, C., Li, H., Du, D., & Lin, Y. (2016). Recent advances in electrochemical biosensors based on graphene two-dimensional nanomaterials. *Biosensors and Bioelectronics*, **76**, 195-212.

[18] Wang, J., Yang, B., Wang, H., Yang, P., & Du, Y. (2015). Highly sensitive electrochemical determination of Sunset Yellow based on gold nanoparticles/graphene electrode. *Analytica Chimica Acta*, **893**, 41-48.

[19] Wang, M., & Zhao, J. (2015). Facile synthesis of Au supported on ionic liquid functionalized reduced graphene oxide for simultaneous determination of sunset yellow and tartrazine in drinks. *Sensors and Actuators B: Chemical*, **216**, 578-585.

[20] Wang, M., Gao, Y., Sun, Q., & Zhao, J. (2014). Sensitively simultaneous determination of sunset yellow and tartrazine in foods based on polypyrrole modified oxidized single-walled carbon nanotubes. *Journal of the Electrochemical Society*, **161**(14), B297-B304.

[21] Wu, X., Zhang, X., Zhao, C., & Qian, X. (2018). One-pot hydrothermal synthesis of ZnO/RGO/ZnO@ Zn sensor for sunset yellow in soft drinks. *Talanta*, **179**, 836-844.

[22] Xu, H., Yang, X., Li, G., Zhao, C., & Liao, X. (2015). Green synthesis of fluorescent carbon dots for selective detection of tartrazine in food samples. *Journal of Agricultural and Food Chemistry*, **63**(30), 6707-6714.