



## Analytical Methods

## Sensitive determination of Amaranth in drinks by highly dispersed CNT in graphene oxide “water” with the aid of small amounts of ionic liquid



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## ABSTRACT

Graphene oxide (GO) is a pH-dependent amphiphile. In this paper, it was found that carbon nanotubes (CNTs) can be highly dispersed in graphene oxide “water” with the aid of prototype ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]). The introduction of [BMIM][PF<sub>6</sub>] not only can minimize the defects of poor electrical conductivity of GO, but also can improve the dispersibility of CNT in water. Hence, a new composite of CNT/GO-[BMIM][PF<sub>6</sub>] with high dispersibility and strong conductivity was presented for the first time and employed in the sensitive determination of Amaranth in soft drinks. The detection limit achieved (0.1 nM) is much lower than the guideline values in soft drinks. The ease of preparation, low background current, high sensitivity and stability can create novel avenues and applications for fabricating robust sensors for determination of other azo dyes in foods.

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## 1. Introduction

Amaranth (FD & C Red No. 2, E 123) is a synthetic azo dye used as a food coloring in foods including soft drinks, cake mixes, ice-creams, wines, salad dressings, chewing gums and chocolates. However, the acceptable maximum addition of Amaranth is strictly fixed because studies have shown that Amaranth could cause many adverse health effects such as high genotoxicity, cytostaticity and cytotoxicity (Mpountoukas et al., 2010; Sarikaya, Selvi, & Erkoç, 2012). The acceptable daily intake (ADI) levels recommended by the Joint Food and Agriculture Organization (FAO)

and World Health Organization (WHO) Expert Committee on Food Additives (JECFA) for Amaranth is 0–1.5 mg/kg (Mpountoukas et al., 2010). In China, the ADI values for Amaranth is 0–0.5 mg/kg based on the FAO and WHO recommendations (Al-Degs, 2009). So determination of Amaranth is of considerable importance. Although electrochemical methods have been successfully developed for the detection of Amaranth, the low sensitivity as well as poor conductivity limited the applied scope of some sensors. Hence, it is important to design electrodes that are sensitive toward the determination of Amaranth.

Owing to its unique structures (Fukushima et al., 2003), large surface to volume ratio and remarkable electrical properties (Atta, Ali, El-Ads, & Galal, 2013; Paul, Choi, Lee, Sudhagar, & Kang, 2012), CNTs have been used extensively in the

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electro-detection (Wang et al., 2010; Zhao, Zhang, Wu, Chen, & Zhou, 2011). However, they are known to be difficult to process in water, which restrict their applications (Fukushima et al., 2003). Hence effective dispersion of CNTs is needed before any further applications can be applied.

Since GO has many  $\pi$ -conjugated aromatic domains in its basal plane, it is able to interact with the CNTs through  $\pi$ - $\pi$  interactions which make it can serve as a dispersing agent for dispersion of CNTs by a simple ultrasonic method (Kim et al., 2010). However, the poor electrical conductivity of GO restricts the applications of CNT-GO composite in the electrochemical detection application (Cai, Song, & Xu, 2008). Therefore, it is useful to test a material to minimize the defects of poor electrical conductivity of GO and also improve the dispersibility of CNT in water.

An interesting option is offered by the prototype IL of [BMIM][PF<sub>6</sub>] which possess high electrical conductivity (Torimoto, Tsuda, Okazaki, & Kuwabata, 2010). [BMIM][PF<sub>6</sub>] are organic salts including cationic structures and typical anions that loosely fit together (Carda-Broch, Berthod, & Armstrong, 2003; Chen, Wu, Sha, & Huang, 2007; Lu et al., 2009). Though ILs can neutralize the charges on the sheets of GO when added to the GO aqueous dispersion. High pH values can promote the deprotonation of the -COOH groups of GO and further make GO more hydrophilic. We found that the GO redispersed in the aqueous phase through adjusting pH to 12.0, forming new aqueous dispersions of GO-[BMIM][PF<sub>6</sub>] water which can remain stable without any precipitation for several months and even longer. So, the introduction of [BMIM][PF<sub>6</sub>] not only minimized the defects of poor electrical conductivity of GO and also improved the dispersibility of CNT in water. And a CNT-GO-IL composite was prepared by a simple and facile ultrasonic method. The method developed here can, not only ensure the conjugated carbon networks of CNT but also can improve the conductivity of the composite. The electrochemical behaviors of Amaranth on the CNT-GO-IL modified electrode were investigated by cyclic voltammetry (CV) and square wave stripping voltammetry (SWSV). The CNT/IL-GO modified electrode showed high sensitivity and perfect selectivity for determination of Amaranth with low detection limits and wide concentration ranges in comparison to CNT/GO modified electrodes. The fabricated electrochemical sensors were further used for practical applications in detection of Amaranth in real samples.

## 2. Materials and methods

### 2.1. Instruments

Cyclic voltammetric (CV) and square wave voltammetry (SWV) measurements were performed with a conventional three-electrode system consisting of a bare or modified glassy carbon electrode (GCE; diameter = 3 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. Scanning electron microscopic (SEM) was running on a Hitachi S-4800 SEM instrument (Japan). Electrochemical impedance spectroscopy (EIS) was performed on an Auto-lab potentiostat/galvanostat (PGSTAT30) with a three-electrode system in PBS (0.1 M) containing K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (5 mM, 1:1) mixture as a redox probe, and recorded at an open circuit potential of 200 mV with an amplitude of 5 mV over a frequency range of 0.01 Hz–100 kHz.

### 2.2. Reagents

Amaranth (95%) was purchased from Aladdin. CNTs (purity > 95%) were prepared from Jiangsu JF Advanced Technologies, Inc. (Nanjing, China). 1-butyl-3-methylimidazolium

hexafluorophosphate ([BMIM][PF<sub>6</sub>]) was purchased from Sinopharm Chemical Reagent Co. (China). Deionized water was applied for all polymerization and reaction processes. A series of 0.1 M Britton–Robinson (BR) buffer solutions of different pH values were prepared by adjusting mixed acid solutions containing phosphoric acid, glacial acetic acid and borax with 1.0 M NaOH. The drinks of Bacardi breezer and Reinbow rum cocktail were purchased from a local market.

GO was synthesized by a modified Hummers' method as reported elsewhere from graphite powder (Hummers & Offeman, 1958). The dry GO filter cakes were redispersed in water to create a stock solution of 1.0 mg/mL, which may be further diluted to various concentrations. The pH value of GO-IL water was modified by adding NaOH (1 M) solution. All other reagents were of analytical grade and used without further purification.

### 2.3. Preparation of the modified electrodes

0.01 g [BMIM][PF<sub>6</sub>] was added to 10 mL of 0.6 mg/mL predispersed GO, all GO precipitate quickly within 10 min for the electrical repulsion between the GO sheets significantly weakened with the addition of this electrolytes (ILs) (Li, Yang, Zhao, & Li, 2013) which includes cationic structures and typical anions (Carda-Broch et al., 2003; Chen et al., 2007; Lu et al., 2009; Wang, Wu, Wu, Lee, Chang, Ger, et al., 2013). Then the pH value of the mixture was turned to 12.0 by adding NaOH (1 M) solution, the mixture was ultrasonicated further in ice-water bath at 99 W for 20-min. It was found that the GO was redispersed in the aqueous phase, forming GO-IL water, because in base solution high pH values can promote the deprotonation of the -COOH groups of GO, which would make GO more hydrophilic (Kim et al., 2010). This can be seen in Fig. S1. After that, 0.20 mg CNTs were added to the GO-IL water and the mixture was ultrasonicated further in ice-water bath at 99 W for 20-min in a similar way. The resulting dispersion, denoted as CNT/GO-[BMIM][PF<sub>6</sub>] (CNT/GO-IL), was collected for further characterizations. Therefore, a new water-processable CNT/GO-[BMIM][PF<sub>6</sub>] composite was conveniently created by a simple and "green" processing route at room temperature.

A glassy carbon electrode (GCE) (surface area 0.07 cm<sup>2</sup>) was carefully polished with alumina powder (grain size, 0.3 and 0.05  $\mu$ m), then ultrasonicated and rinsed with nitric acid (1:1, v/v), ultrapure water and acetone to remove any alumina residue from the electrode surface. For the detection of Amaranth, a drop of CNT/GO-[BMIM][PF<sub>6</sub>] dispersion (5.0  $\mu$ L) was dropped onto the surface of the pretreated GCE (denoted as GO/CNT-IL/GCE) and dried in air under 70 °C by infrared lamp for 10 min. For comparison, CNT and CNT/GO modified GCE was also fabricated with the similar procedures.

### 2.4. Analytical procedure

Unless otherwise stated, 0.1 M BR buffer with pH of 7.0 was used as the supporting electrolyte for the detection of Amaranth. Square wave stripping voltammetry (SWSV) was employed for the detection of Amaranth with scan range from 0.4 to 1.0 V. After 360 s accumulation, the square wave voltammograms were recorded from 0.4 to 1.0 V, and the oxidation peak current at 0.704 V was measured as the analytical signal for Amaranth.

### 2.5. Sample detection

Different fruit drink samples were purchased from a local market and used directly without any pretreatment. 0.2 mL sample solution was added into 20.0 mL pH 7.0 BR buffer solutions and analyzed according to the above analytical procedure.

### 3. Results and discussion

#### 3.1. Characterization

The surface morphology of the composite material was examined by scanning electron microscope (SEM). Fig. 1A displays the SEM image of CNT. It can be seen that the CNTs samples were heavily entangled, which remained largely unaffected by sonication in water. SEM images of CNTs sonicated in GO water showed that most of CNTs are covered by GO (dark area) (Fig. 1B). While extensive microscopy observations by SEM revealed that almost all the CNTs are well dispersed and disentangled in GO-[BMIM][PF<sub>6</sub>] water (Fig. 1C) and nearly all the CNTs in the sample were adhered to GO. Only individual tubes or bundles of a few tubes were found. So the introduction of [BMIM][PF<sub>6</sub>] to GO water improved the dispersibility of CNT to a large extent. In addition, the energy dispersive X-ray (EDX) spectrum of CNT/GO-[BMIM][PF<sub>6</sub>] is shown in Fig. S2 which confirm the formation of CNT with [BMIM][PF<sub>6</sub>]-GO hybrid material.

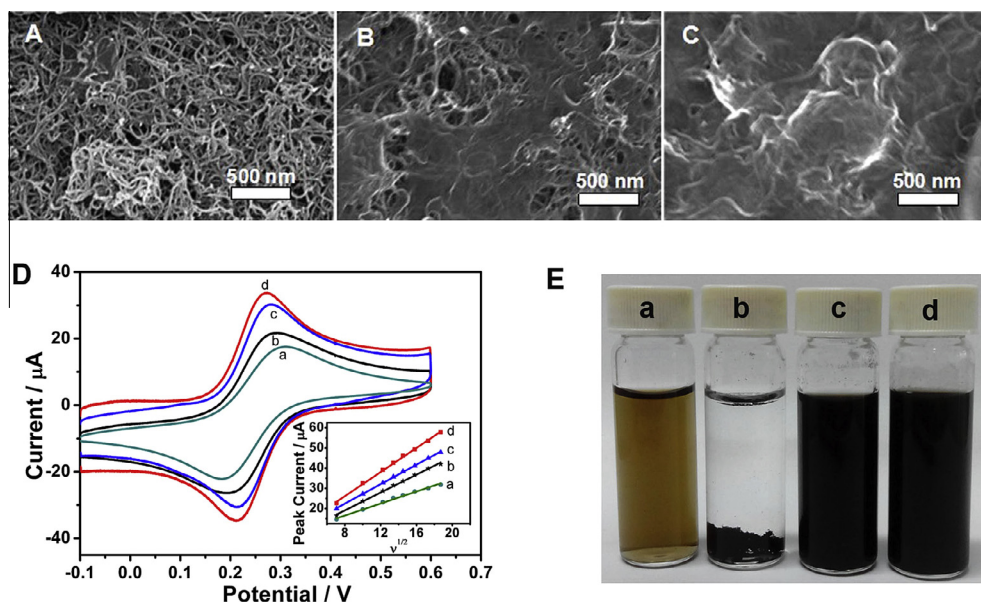
Fig. 1D compares the CVs of bare GCE, CNT/GO or CNT/GO-IL composite modified GCE in the aqueous solution of 2 mM ferrocyanide and 1.0 M KCl. Each CV cycle shows a couple of oxidation and reduction waves due to the redox of Fe<sup>3+</sup>/Fe<sup>2+</sup>. It is clear from Fig. 1D that the CV wave current densities of the modified GCE are higher than those of the bare GCE, indicating that the modified electrodes have enhanced electro-catalytic activity. Especially, the CV wave currents of the CNT/GO-IL modified electrode are much stronger than those of the CNT/GO modified electrode. Furthermore, the CV peak separation of the CNT/GO-IL modified electrode is obviously lower than that of the CNT or CNT/GO modified electrode which is mainly due to the introduction of the IL. The Nyquist diagrams of EIS for GO modified GCE (GO/GCE) and GO-[BMIM][PF<sub>6</sub>] modified GCE (GO-IL/GCE) are presented in Fig. S3. The electric conductivity of the two electrodes was similar. However, electron transfer rate of ferri/ferrocyanide redox reaction was larger at the GO-IL than the GO modified electrode (Zhang et al., 2012).

Obviously, the introduction of [BMIM][PF<sub>6</sub>] can cause fast electron transfer rate of Amaranth at modified electrode and is benefit for the sensitive determination of Amaranth.

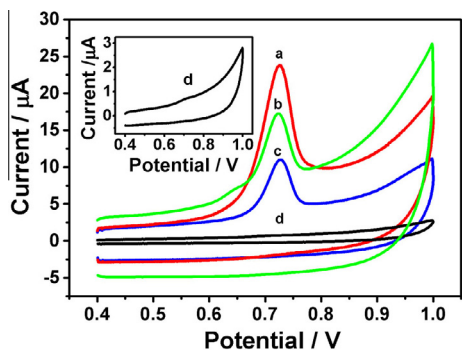
The effective surface area is a crucial factor influencing the Amaranth adsorbed amount and the electrochemical response (Fig. 1D inset), which was evaluated by Randles–Sevcik equation using K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> as an indicator (Jiang & Wang, 2009; Sun, Qin, Zhao, & Jiao, 2010):  $I_p = (2.687 \times 10^5) n^{3/2} v^{1/2} D^{1/2} AC$  (Jiang & Wang, 2009), where  $n=1$ ,  $v$  is scan rate (V s<sup>-1</sup>),  $D = 5.7 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> and  $C$  is the concentration (mol cm<sup>-3</sup>) of the K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub>; The effective surface area ( $A$ ) is proportional to  $I_p/v^{1/2}$  which is shown in the inset of Fig. 1D. The effective surface area of CNT/GO-IL modified GCE increased for 1.5 times than that of CNT/GO modified GCE, confirming that the introduction of IL further decreased the aggregation of CNTs. Fig. 1E shows the photographs of aqueous dispersions of GO (a), CNT (b), CNT/GO (c) and CNT/GO-IL (d) taken 24 h after ultrasonication. It is clearly seen from this figure that the CNTs were suspended in water eventually settled down after a period time. The addition of GO resulted in a black colloidal dispersions with no visible precipitation. Also there was no sediment observed in the vial of CNT/GO-IL. The colloidal dispersion of CNT/GO and CNT/GO-IL was found to be stable even after a long aging time.

#### 3.2. Electrochemical behaviors of Amaranth on CNT/GO-IL modified GCE

The electrochemical behaviors of Amaranth was carefully investigated at the bare GCE, CNT/GCE, CNT/GO/GCE and CNT/GO-IL/GCE using CV. Fig. 2 shows the cyclic voltammograms of the 1.0 μM Amaranth in 0.1 M BR (pH 7.0). At the unmodified GCE, little oxidation peak is observed for Amaranth even after 6-min accumulation (curve d), suggesting that the determination of Amaranth using GCE was difficult. Although the peak also occurred at CNT/GCE (curve c) and CNT/GO-GCE (curve b), the comparison reveals that the oxidation current obtained at the CNT/GO-IL/GCE (curve a) is greatly enhanced compared with that at the CNT/GO-GCE and



**Fig. 1.** SEM images of CNT after sonication in DI water (A), CNT after sonication in GO water (B) and CNT after sonication in GO-IL water (C). Cyclic voltammograms of bare GCE (a), CNT (b), CNT/GO (c), CNT/GO-IL (d) modified GCE in a 2 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 M KCl solution at a scan rate of 100 mV s<sup>-1</sup>; inset: peak currents as a function of scan rate for the determination of the effective working surface area (D). Photographs of GO (a), CNT (b), CNT/GO (pH = 7.0) (c) and CNT/GO-IL composite (pH = 12.0) (d) dispersed in water after 20 min ultrasonication and stand for 24 h (E).



**Fig. 2.** Cyclic voltammograms of 1.0  $\mu\text{M}$  Amaranth in pH 7.0 BR at different electrodes: CNT/GO-IL/GCE (a), CNT/GCE (b), CNT/GO/GCE (c) and GCE (d). Scan rate: 100  $\text{mV s}^{-1}$ .

resulted in a decrease in background current. These observations indicate a faster electron-transfer rate for the oxidation of Amaranth at the CNT/GO-IL modified GCE which was attributed to the improved conductivity, high dispersibility and increased effective surface area of the composite. This can in favor of more Amaranth accumulated to the working electrode in the accumulation process.

### 3.3. Optimization of the condition for the electrode fabrication

The amount of CNT/GO-IL composite for the fabrication of CNT/GO-IL/GCE was one important parameter affecting the performance which was evaluated by SWSV. As shown in Fig. 3A, with an increasing amount from 2.5 to 5.0  $\mu\text{L}$ , the oxidation peak currents of Amaranth increased, afterwards the response decreased

as the amount further increased, which was caused by hindering fast electron transport due to excessive of composites on the electrode surface. Therefore, 5.0  $\mu\text{L}$  CNT/GO-IL was an optimal amount used for modified the GCE.

### 3.4. Optimization of detection variables

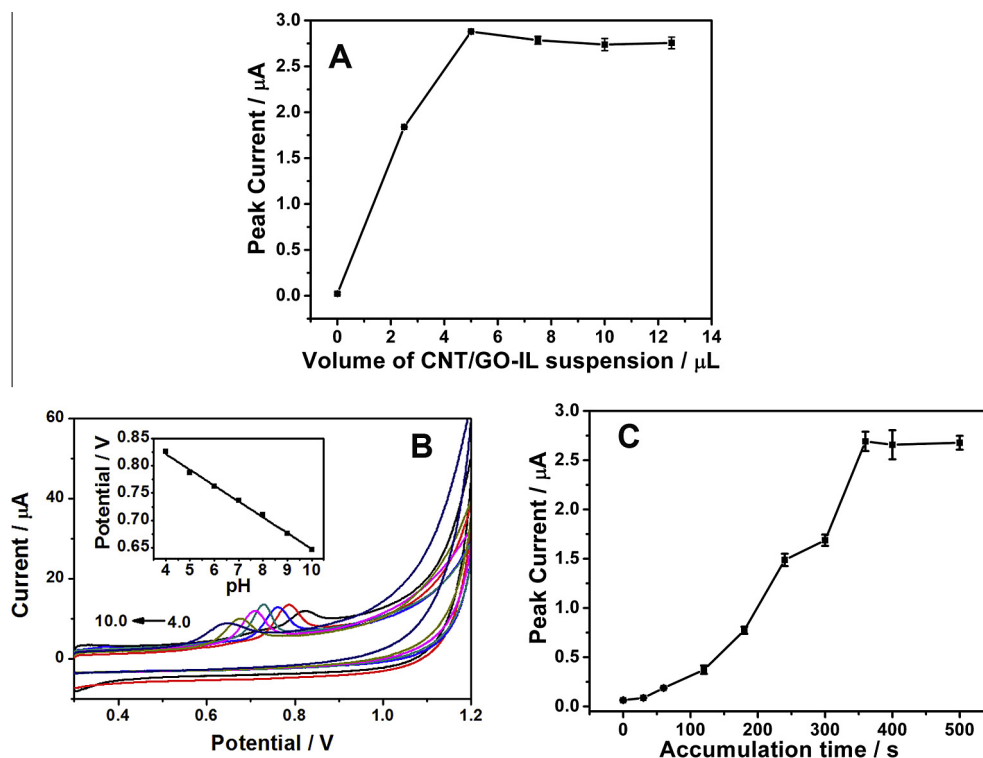
#### 3.4.1. Effect of pH

Fig. 3B displays the effect of pH on the oxidation peak currents of 1.0  $\mu\text{M}$  Amaranth at the CNT/GO-IL/GCE. With the increasing pH from 4.0 to 7.0 the currents increased, afterwards the currents decreased as pH further increased.

Therefore, the optimal pH 7.0 was chosen for subsequent electrochemical determination of Amaranth. In addition, the relationship between the oxidation peak potentials of Amaranth and pH was also constructed. As shown in the inset of Fig. 3B, with the increasing pH from 4.0 to 10.0, the oxidation peak potentials of Amaranth linearly shifted to more negative potential. The regression equations for Amaranth was  $E_{\text{pa}} (\text{V}) = -0.029 \text{ pH} + 0.938$  ( $R = 0.997$ ), indicating that protons are directly involved in the oxidations of Amaranth. The slopes of the function of  $E_{\text{pa}}$  vs. pH deviated from the theoretical value, it could be ascribed to the influence of the slower electrode reaction (Mo et al., 2010).

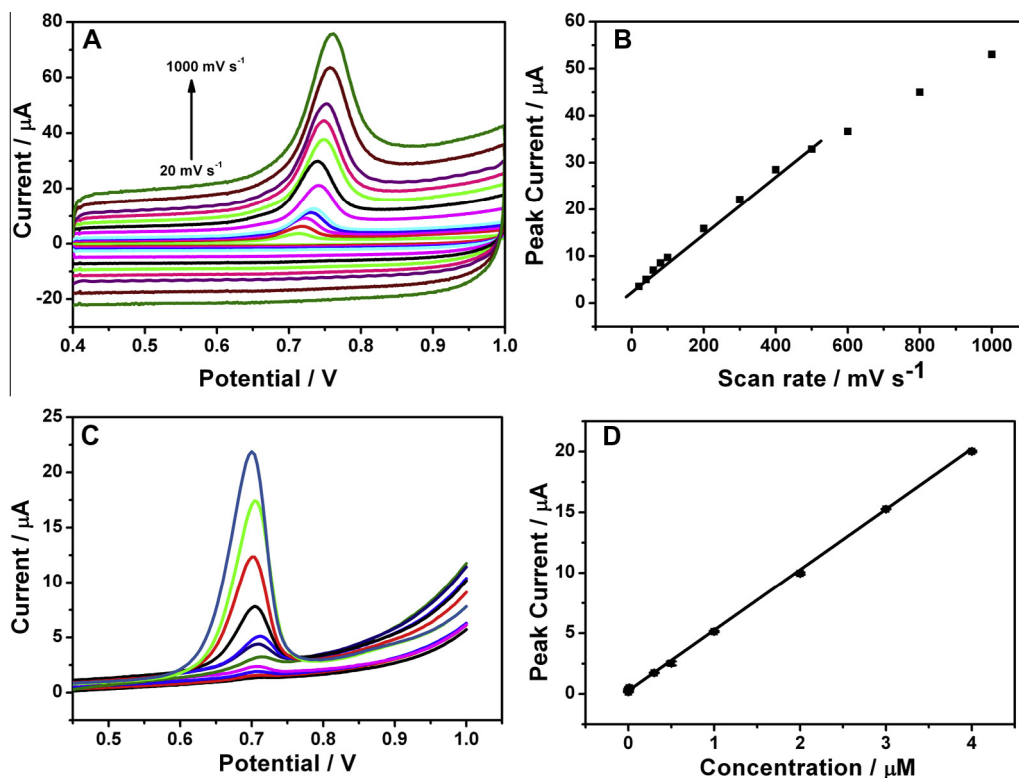
#### 3.4.2. Effect of accumulation parameters

For handling convenience and further improving the sensitivity, accumulation was conducted at different initial potentials when detecting Amaranth. The peak current of the Amaranth was almost independent of the initial potential. To achieve high sensitivity and excellent oxidation shape, the SWV sweep started from 0.4 V. The influence of accumulation step on the oxidation peak current of 0.5  $\mu\text{M}$  Amaranth was investigated. The oxidation peak currents of Amaranth after 6-min accumulation under different accumula-

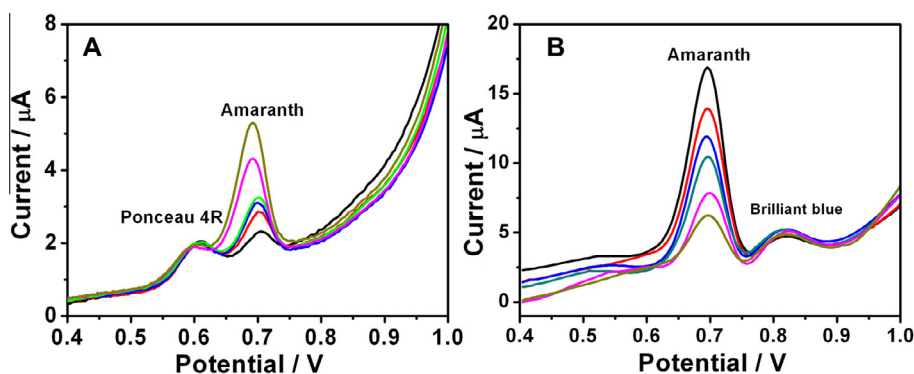


**Fig. 3.** Effects of mass volume of CNT/GO-IL on the oxidation peak current of 0.5  $\mu\text{M}$  Amaranth (A). Effects of pH values on the oxidation peak current and peak potential (inset) of 1.0  $\mu\text{M}$  Amaranth (B). Oxidation peak currents of 0.5  $\mu\text{M}$  Amaranth as a function of accumulation time. Error bar represents the standard deviation of triple measurements (C).





**Fig. 4.** Effect of scan rate on the redox behavior of 1.0  $\mu\text{M}$  Amaranth (0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0  $\text{V/s}$ ) (A). Plot of peak current density vs. scan rates for Amaranth (B). SWV curves of 0.0005–4.0  $\mu\text{M}$  Amaranth on the CNT/GO-IL/GCE in 0.1 M BR solutions (pH 7.0) (C). Plot of the oxidation peak current against the concentration of Amaranth. The error bar represents standard deviations for three tests (D).



**Fig. 5.** (A) SWVs of the CNT/GO-IL/GCE at pH 7.0 BR buffer containing different concentrations of Amaranth (from inner to outer): 0.04, 0.06, 0.08, 0.1, 0.15 and 0.2  $\mu\text{M}$  and 0.015  $\mu\text{M}$  Ponceau 4R. (B) The SWVs of different concentrations of Amaranth (from inner to outer): 0.5, 0.8, 1.0, 1.2, 1.5 and 2.0  $\mu\text{M}$  and 1.0  $\mu\text{M}$  Brilliant blue.

**Table 1**  
Determination of Amaranth in the Bacardi breezer and Reinnow rum cocktail drinks.

Samples	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	RSD (%)	Recovery (%)
Bacardi breezer	0.02	0.02	1.00	100.0
	0.04	0.041	1.38	102.5
	0.1	0.105	3.34	105.0
Reinnow rum cocktail	0.02	0.019	2.01	95.0
	0.04	0.039	2.43	97.5
	0.1	0.099	2.01	99.0

tion potentials containing  $-0.4$ ,  $-0.3$ ,  $-0.2$ ,  $-0.1$ ,  $0$ ,  $0.2$ ,  $0.4$ ,  $0.5$ ,  $0.6$  and  $0.7$  V, and open-circuit were measured. The peak current of the Amaranth was almost independent of the accumulation potential, and values of relative standard deviation (RSD) of the peak currents

of the Amaranth were less than 3.1%. This result indicated accumulation potential had no obvious influence on the oxidation reaction of Amaranth. Thus, the accumulation step was performed under open-circuit.

Fig. 3C shows the variation of peak currents of 0.5  $\mu\text{M}$  Amaranth with respect to accumulation time under open-circuit on the CNT/GO-IL/GCE. The peak current of Amaranth improved with accumulation time, but after 360-s remained almost constant. This may be due to saturation of the Amaranth adsorbed on the modified electrode.

#### 3.4.3. Effect of scan rate

The effects of scan rate on the current of 1.0  $\mu\text{M}$  Amaranth were investigated. Fig. 4A shows the cyclic voltammograms of Amaranth at different scan rates. It can be seen the CNT/GO-IL/GCE shows an

irreversible oxidation peak for Amaranth, and the oxidation peak current of Amaranth increase linearly over the range of 20–500 mV s<sup>-1</sup> while deviates from linearity from 600 to 1000 mV s<sup>-1</sup> (Fig. 4B), indicating absorption process changing to diffusion process (Wang, Gao, Sun, & Zhao, 2015; Wang et al., 2014) of Amaranth at the CNT/GO-IL/GCE surface.

### 3.5. Analytical properties

#### 3.5.1. Linear range and detection limit

The SWV in Fig. 4C shows the relationship between oxidation peak currents against the concentration of Amaranth in 0.1 M pH 7.0 BR buffer solutions. It can be seen in Fig. 4D that the oxidation peak current varies linearly with the concentration of Amaranth in the range of  $5.0 \times 10^{-10}$  to  $4.0 \times 10^{-6}$  M and the regression equations can be expressed as  $I$  (μA) =  $4.92 C$  (μM) + 0.1857 ( $R^2 = 0.999$ ) with detection limit of 0.1 nM. The LOD of the present system is lower. The result of CNT/GO-IL composite modified GCE detection platform is compared with other published works (Han et al., 2014; Wang, Zhang, Ding, Zhu, & Chen, 2013; Wang et al., 2010; Zhang, Gan, Wan, & Wu, 2013) (Table S1). It is obvious that the prepared sensor is more sensitive, and has a lower LOD toward Amaranth, which provides an attractive perspective for its wide application.

#### 3.5.2. Reproducibility, stability and reusability

The reproducibility of the CNT/GO-IL/GCE was examined at the solution containing of  $5.0 \times 10^{-7}$  M Amaranth, and the relative standard deviations (RSDs) of current signals at six independently CNT/GO-IL/GCE were 2.01%, proving accept reproducibility. 90.3% of the initial response of the electrode for Amaranth was remained after three weeks when using once per 5 days, indicating good stability.

The regeneration of the CNT/GO-IL/GCE was developed by cycling voltammetric from 0.3 to 1.0 V in 0.1 M pH 7.0 BR buffer solution for 20 times. The as-renewed CNT/GO-IL/GCE could restore 97.2% of the initial value for Amaranth after 6 assay runs, showing high reusability.

#### 3.5.3. Interference

The interference of several potentially interfering species on the determination of Amaranth was investigated by SWSV under the above optimized conditions. The oxidation peak currents of  $1.0 \times 10^{-7}$  M Amaranth after a 360-s accumulation in the presence of various concentrations of foreign species were measured. The results suggesting 1000-fold concentration of sucrose, saccharin, glucose and vitamin C; 500-fold concentration of sodium citrate, oxalic acid, sodium oxalate; 100-fold concentration of  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $Cl^-$ ; and 20-fold concentration of Quinoline yellow and ten-fold concentrations of Tartrazine have no influence on the determination of Amaranth. The same concentrations of Sunset yellow had an intense negative effect on the square-wave stripping voltammetry response of Amaranth because its oxidation peak potential was similar to that of Amaranth at pH 7.0. Fig. 5A and B shows the SWV responses which were gained by varying the concentration of Amaranth while the concentrations of Ponceau 4R (A) or Brilliant blue (B) was kept constant. Obviously, the Ponceau 4R and Brilliant blue did not influence the determination of Amaranth. So the CNT/GO-IL/GCE also may be used to simultaneously determination of Ponceau 4R, Amaranth and Brilliant blue in drinks.

#### 3.5.4. Application in soft drinks analysis

To evaluate the potential application, the proposed method was applied to the detection of Amaranth by the standard addition method in Bacardi breezer and Reinnbow rum cocktail drink samples. Recovery testing was carried out to demonstrate the

validity of the proposed method. The recovery of the spiked samples ranged from 95.0% to 105.5%, and the RSD ( $n = 5$ ) was less than 4.0% (Table 1). This indicates that the fabricated electrochemical sensors could satisfy the need for determination of Amaranth in soft drinks and has promising application.

### 4. Conclusions

In summary, we have fabricated, for the first time, a sensitive, stable, and robust electrode modified by CNT/GO-[BMIM][PF<sub>6</sub>], for the specific detection of Amaranth in fruit drinks. The new composite material combines the unique and attractive electro-catalytic behavior of carbon nanotubes and the IL of [BMIM][PF<sub>6</sub>] with very low background current toward the Amaranth. In addition, the composite modified electrode possess larger effective surface area and high sensitivity, can be applied to fruit drinks, and worked well over a broad linear range with a low detection limit (0.1 nM) toward the Amaranth, demonstrating the resiliency of this method to endogenous interferences in fruit drinks. The sensor also has the advantages of low cost, high specificity, and reproducibility, which makes it a promising tool for determination of other azo dyes in foods. We believe this composite material can be further used for unlimited number of applications with outstanding performance.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2015.01.143>.

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