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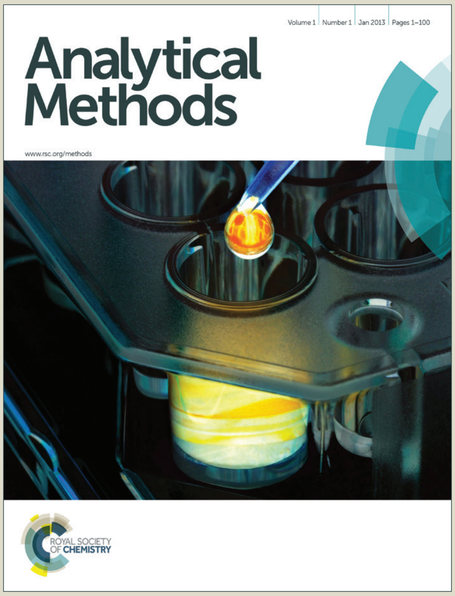

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Determination of Sunset yellow in foods based on a facile electrochemical sensor

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Abstract: A new electrochemical sensor to determine Sunset yellow (SY) in foods has been developed. A composite consisting of highly dispersed polypyrrole (ppy) and single-walled carbon nanotube (ppy-SCNT) was synthesized as modifications by a facile method at room temperature. The ppy-SCNT composites were demonstrated to be highly sensitive for SY detection. The influences of pH value, amount of ppy-SCNT dispersion, accumulation time and scan rate on the signal enhancement of SY were discussed. Under optimal experimental conditions, the ppy-SCNT modified glass carbon electrode (ppy-SCNT/GCE) exhibited a wide linear response to SY ranging from 2.0×10^{-9} to 1.5×10^{-6} M with a high sensitivity of 91.53 μA/μM and a low detection limit down to 3.0×10^{-10} M (S/N=3). The novel ppy can prevent the aggregation of SCNT *via* π-π interaction, and enhance their electrochemical properties in the measurement of Sunset yellow in food samples. The novel sensor possess following features: facile fabrication, easy operation and acceptable stability. The analysis of real sample drinks demonstrated that the electrode owns excellent selectivity.

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1 Introduction

In the recent years, synthetic colorant Sunset yellow (Fig. 1) is widely used as additives in foodstuffs such as soft drinks, potable spirit, candies, chocolate and jelly in order to make them more visually attractive to consumers which has been the most popular object in the food chemistry analytical field. This hot trend is driven by not only the well-known rising demands for food monitoring and safety, but also the urgent requirements for guaranteeing the safety of consumers especially children [1]. Reports suggest that dietary exposure of SY would produce some adverse effects on several behavioral developmental parameters during the early lactation period [2-4]. In a recent study, it was also found that synthetic colorant SY consumed excessively would exert a depressing effect on the cellular and predispose to neuro toxicity in young and adult animals [5]. Due to this, the use of synthetic colorants SY in foods is strictly controlled by laws and regulations. The acceptable daily intake (ADI) values for SY are 0 to 2.5 mg kg^{-1} body weight (JECFA, 1982) [2].

And it has attracted tremendous academic efforts to develop different kinds of methods such as high-performance liquid chromatography (HPLC) [6-11] and spectrophotometry methods [12-14]. However, HPLC has some deficiencies such as costly equipment, tedious and time-consuming procedures or in need of specially trained operators. The spectrophotometry typically suffers from relatively low detection limits and poor sensitivity. This fact has encouraged chemists to develop faster, easier, and more sensitive methods to meet the demands. In recent years, electrochemical method has been revealed as promising tools for the determination of SY [15-18] and it also has been recognized as the most convenient and effective tool for SY analysis to date. Furthermore, electrochemical determination of SY has been proposed based on various chemically modified electrodes [15-17, 19-21]. In this work, we present a facile strategy to fabricate a polypyrrole/single-walled carbon nanotube (ppy-SCNT) composites modified electrode in the electrochemical analysis of SY.

Since the discovery of carbon nanotube (CNT) in 1991 by Iijima [22], it has exhibited good chemical and thermal stability, high electrical conductivity and large surface area [23-26]. It has also been reported that CNT has shown good prospects as a potential electrode modifying material in recent years [27-29]. In spite of having ideal properties, the specific surface areas of pure CNT are low because CNT tend to form irreversible agglomerates or even restack, leading to a low dispersibility and poor performance in application. Much effort has gone into preventing the accumulation of CNT based materials, such as compositing conductive polymers with CNT.

Polypyrrole (ppy), as one of the important conducting polymers, has been extensively studied because of its ease of formation, high conductivity, and low cost [30, 31]. Composite materials based on the coupling of conducting polymers and CNTs have complementary characteristics of the individual components with a synergistic effect [32]. A few works have been done in synthesis of ppy/CNT composites [33-35]. Among the variety of synthesized methods, the chemical oxidative polymerization stands out as being one of the most widely used methods [36-38]. However, dilute acids was usually used as reaction media and $FeCl_3$, KIO_3, or $K_2Cr_2O_7$ were usually employed as oxidants in the typically used chemical oxidative polymerization process [36-38]. In the present study, ppy-SCNT composites were fabricated via chemical oxidative polymerization of pyrrole in the presence of the single walled carbon nanotubes where ppy was synthesized through a milder approach using ferrous chloride ($FeCl_2$), and green oxidant H_2O_2 as catalysts at room temperature which was a modified method. The ppy prevent the aggregation of SCNT successfully, which lead to a high dispersibility of ppy-SCNT composites. The ppy-SCNT dispersion is found to have high electrocatalytic activity towards the oxidation of SY.

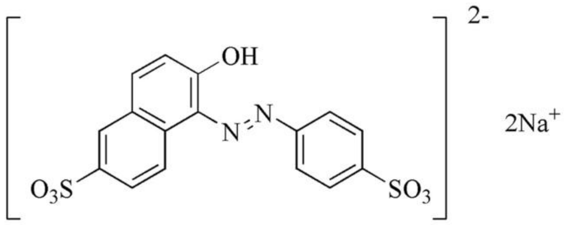

Fig. 1 The molecule structure of the Sunset yellow.

2 Experimental

2.1 Apparatus and Reagents

Pyrrole (AR) and hydrogen peroxide (H_2O_2, 30%, AR) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). $FeCl_2$ (80%, AR) were purchased from Shanghai Chemical Reagent Co. (China). SCNTs (purity > 95%) were prepared from Jiangsu JF Advanced Technologies, Inc. (Nanjing, China). Deionized water was applied for all polymerization and reaction processes. Sunset yellow was purchased from Aladdin, and dissolved into deionized water to prepare 1×10^{-3} M standard solution. The food samples of jelly and fruit drink were purchased from a local market. 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.

Square wave voltammetry (SWV) and cyclic voltammetric (CV) 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 Autolab potentiostat/galvanostat (PGSTAT30) obtained from Eco Chemie B.V., (Utrecht, Netherlands) with a three-electrode system in KCl solution (0.5 M) containing $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (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 0.05 Hz-10000 Hz. X-ray photoelectron spectroscopy (XPS) measurements are performed on a PHI 5000 VersaProbe.

2.2 Preparation of ppy-SCNT Composites

The synthesis of ppy-SCNT composites was according to a modified method [39, 40]. After adding 0.5 mL H_2O_2 and 0.01 g $FeCl_2$ to the SCNT/pyrrole/H_2O (0.03 g/0.1 mL/50 mL) mixture and lasted for 12 h, then dispersed in water at a concentration of 0.2 mg/mL.

2.3 Fabrication of the Modified Electrode

For the detection of SY, 10 μL of ppy-SCNT composites dispersion was dropped on the surface of GCE and dried by infrared lamp. For comparison, SCNT/GCE was fabricated with the similar procedures, respectively.

2.4 Experiment Procedures

The electrochemical behavior of SY was firstly conducted by CV method in a standard three-electrode reactor. The analytical procedure mainly contains two steps: accumulation step and determining step. The prepared modified electrode was firstly immersed in the BR (0.1 M, pH 7.0) buffers containing 5×10^{-7} M of SY stock solutions and the SY were accumulated to the modified electrode biased at open circuit for 300 s while stirring the mixed solution. After the pre-concentration period and the stripping stopped, CVs were obtained from 0.3 V to 1.0 V after 30 s of equilibrating time. SWV measurements were also recorded with the same two steps to gain the calibration curves, and the oxidation peak currents at 0.68 V was measured for SY. The amplitude is 25 mV, the frequency is 10 Hz and the potential incremental is 4 mV. Before or after every measurement, the electrode can be regenerated by cycling voltammetric from 0.3 V to 1.0 V in 0.1 M pH 7.0 BR solution for 20 times.

3 Results and Discussion

3.1 Characterization of ppy-SCNT

Fig. 2 displays the typical SEM images of SCNT and ppy-SCNT composites. The pristine SCNT showed a typically smooth surface (a). By contrast, the surface of SCNT is rougher after the decoration of ppy (b). Fig. 3a shows the XPS patterns of SCNT and SCNT-ppy composites. It is shown that, the peak of N1 s in the SCNT-ppy composites was obviously observed, which were in a good agreement with the result of SEM, suggested the presence of ppy in the concerned composite. That oxygen containing groups are incorporated into the composites were also demonstrated. It can be seen from Fig. 3b that the composite possess high dispersibility after decorating ppy on the surface of SCNT which resulted in high performance of the composite in the following experiments.

3.2 Electrochemical Behaviors of SY on the Modified Electrode

The advantages of the usage of ppy-SCNT composites are demonstrated by CV (Fig. 4).

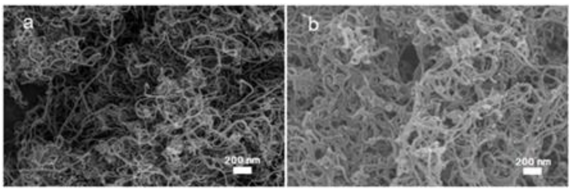

Fig. 2 SEM images of SCNT (a) and ppy-SCNT composites (b).

The comparison showed that the oxidation peak potential of SY at the ppy-SCNT/GCE (curve c) shifted to 0.686V, much lower than that at the bare GCE (0.701 V) (curve a). In addition, compared with at the SCNT/GCE (curve b), the peak current of SY at the ppy-SCNT/GCE showed a remarkable enhancement. The results could be reasonably ascribed to the high dispersibility of the composites. In addition, the effective surface area is also a crucial factor influencing the SY amount adsorbed to the working electrode [41] and the ppy-SCNT/GCE exactly possessed high accumulation efficiency which was demonstrated through electrochemical behaviors of different modified electrode in 0.5 M KCl solution containing 2 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (Fig. 5). This was evaluated by Randles-Sevcik equation [42, 43] : $I_p = (2.687\times10^5)\ n^{3/2}\ \upsilon^{1/2}\ D^{1/2}\ AC$ and ferricyanide was used as an indicator, where n=1 C represent the concentration (mol cm^{-3}) of the ferricyanide; $D = 5.7\times10^{-6}$ $cm^2\ s^{-1}$ [40]; υ is scan rate (V s^{-1}) and A is the surface area (cm^2). The surface area of bare GCE calculated to be 0.070 cm^2, compared well with the geometric area of 0.071 cm^2. The calculated effective surface area of the SCNT/GCE and ppy-SCNT/GCE were 0.090 and 0.110 cm^2, respectively. So the effective surface area of ppy-SCNT/GCE was increased for 1.57 times than that of GCE, confirming that the introduction of ppy indeed increased the effective surface area of the working electrode. So the excellent performance of SY at the ppy-SCNT/GCE resulted from large effective surface area of the modified electrode.

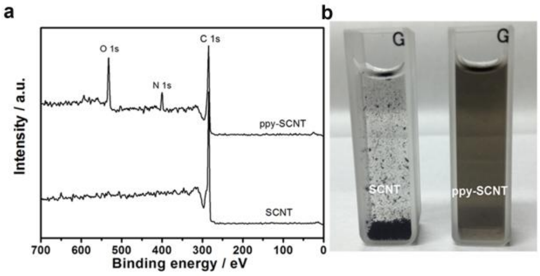

Fig. 3 (a) XPS spectra of SCNT and ppy-SCNT composite. (b) Photographs of pure SCNT and ppy-SCNT composite after ultrasonication 30 min in water and a stand for 1 h.

Fig. 6 shows the Nyquist diagrams of electrochemical impedance spectroscopy (EIS) for bare GCE, SCNT/GCE and ppy-SCNT/GCE, respectively. The semicircle diameter is related to electron-transfer resistance (Ret), which is a measure of the charge transfer kinetics. It was clear that the Ret value of SCNT/GCE was lower than ppy-SCNT/GCE. Obviously, the decoration of ppy on SCNT didn't improve the conductivity of the electrode which may be due to the introduction of oxygen containing groups demonstrated from XPS analysis (Fig. 3a). This outcome further indicates that excellent performance of the ppy-SCNT/GCE toward the SY attributed to the high dispersibility and increased effective surface area of the composite.

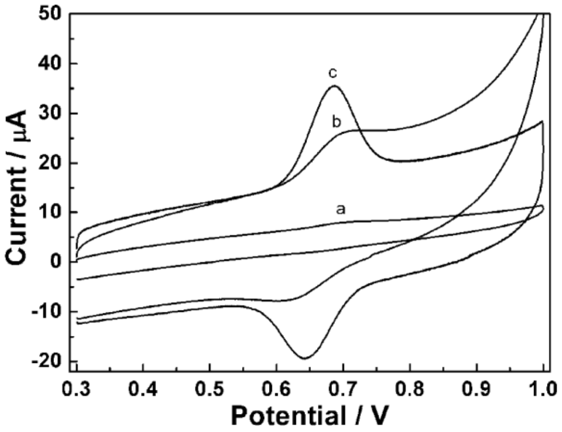

Fig. 4 Cyclic voltammograms of SY at bare GCE (curve a), SCNT/GCE (curve b) and ppy-SCNT/GCE (curve c).

3.3 Optimization of the Experimental Conditions

3.3.1 Effect of the Amount of ppy-SCNT

The dependence of ppy-SCNT amount on the amperometric response of SY was investigated in this work. When increasing the volume of ppy-SCNT suspension to 10 μL, the surface amount of ppy-SCNT also increases, leading to larger surface area and higher accumulation efficiency toward SY, afterwards the response decreased as the suspension further increased in the range of 10-15 μL. Therefore, 10 μL of suspension was an optimal modified amount for amperometric measurement

3.3.2 Effect of Accumulation Parameters

To learn more about the adsorption of SY to the ppy-SCNT/GCE, the oxidation peak current of SY after 5-min accumulation under different accumulation potentials as well as open-circuit were measured. The peak current of the SY oxidation was almost independent of the accumulation potential, indicating accumulation potential had no obvious influence on the oxidation reaction of SY. The peak current of SY improved with accumulation time under open-circuit, but after 300 s remained almost constant. This may be due to saturation of the amount of SY adsorbed on the modified electrode surface.

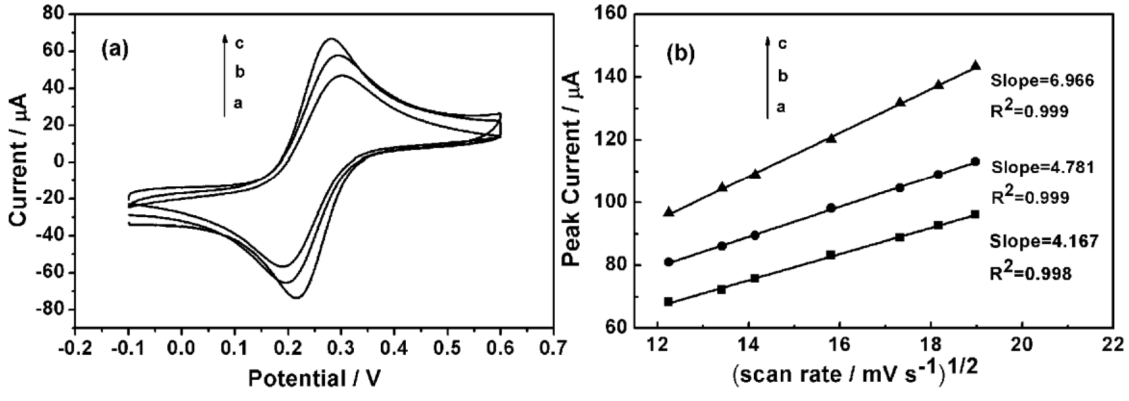

Fig. 5 (a) Cyclic voltammograms of bare GCE (curve a), SCNT/GCE (curve b), and ppy-SCNT/GCE (curve c) in a 0.5 M KCl solution containing 2.0 mM $[Fe(CN)6]^{3-/4-}$ at a scan rate of 100 mV s^{-1}, (b) Peak currents as a function of scan rate for the determination of the effective working surface area.

3.3.3 Effect of pH Values

CVs of SY were recorded with 0.1 M BR buffer solution of various pH values from 3.0 to 11.0. The highest oxidation peak current is obtained in BR solution of pH 7.0. Hence 0.1 M BR with pH 7.0 is selected as supporting electrolyte for further studies throughout.

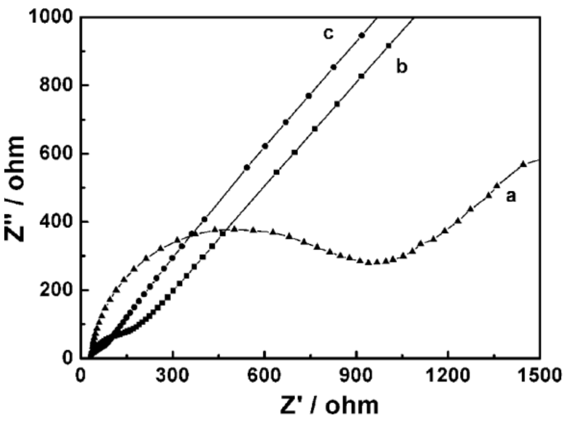

Fig. 6 Nyquist plots of the electrochemical impedance spectroscopy (EIS) for bare GCE (curve a), SCNT/GCE (curve c) and ppy-SCNT/GCE (curve b) in a 0.5 M KCl solution containing 2.0 mM $[Fe(CN)_6]^{3-/4-}$.

3.3.4 Effect of the Scan Rate

The effects of scan rate on oxidation peak potential and current of SY were investigated at ppy-SCNT/GCE. Fig. 7a shows the cyclic voltammograms of SY at different scan rates (5 mV-1000 mV s^{-1}). It can be seen from Fig. 7c that both the anodic and cathodic peak current increase linearly over the range of 5-400 mV s^{-1}. And the regression equation can be expressed as: Ipa (μA) = 5.012+0.275 υ (mV s^{-1}) (R^2=0.995) and Ipc (μA) = -5.323-0.212 υ (mV s^{-1}) (R^2=0.994), respectively. In addition, the current increases slowly at scan rates between 400 and 1000 mV s^{-1} and deviates from linearity (Fig. 7d) which strongly suggested that the probable mechanism of electrode reaction of SY was changed gradually from the absorption of SY at the modified electrode surface into the diffusion to the electrode surface. On the other hand, with the increase of scan rates, the plot of E_p versus the logarithm natural of scan rate showed a linear behavior in Fig. 7b for SY in the range of 100-400 mV s^{-1}, which is in agreement with the Laviron theory [44]: a plot of E_p versus lnν yields two straight lines with slopes of -RT/αnF and RT/(1-α)nF. The α value of SY can be evaluated as 0.47 from the slopes of linear and the value of n estimated as 1.32 indicating that one electrons was involved in the oxidation of SY based on the following Laviron equation:

$$E_a = E^o + \frac{RT}{(1-\alpha)nF} \ln[\nu(1-\alpha)nF / RTk_s]$$

$$E_c = E^o - \frac{RT}{\alpha nF} \ln(\nu\alpha nF / RTk_s)$$

where F is the Faraday constant; k_s is the heterogeneous electron transfer rate constant; E^o is the conditional potential; ν, R and T represent their usual meaning. And the k_s value can be evaluated as 5.33 s^{-1}. The smaller value of ks further indicates that the electron transfer velocity is so slow that it's too late for SY to take reaction at the surface of the electrode at high scan rates, which best explain why the current of SY deviates from linearity at high scan rates.

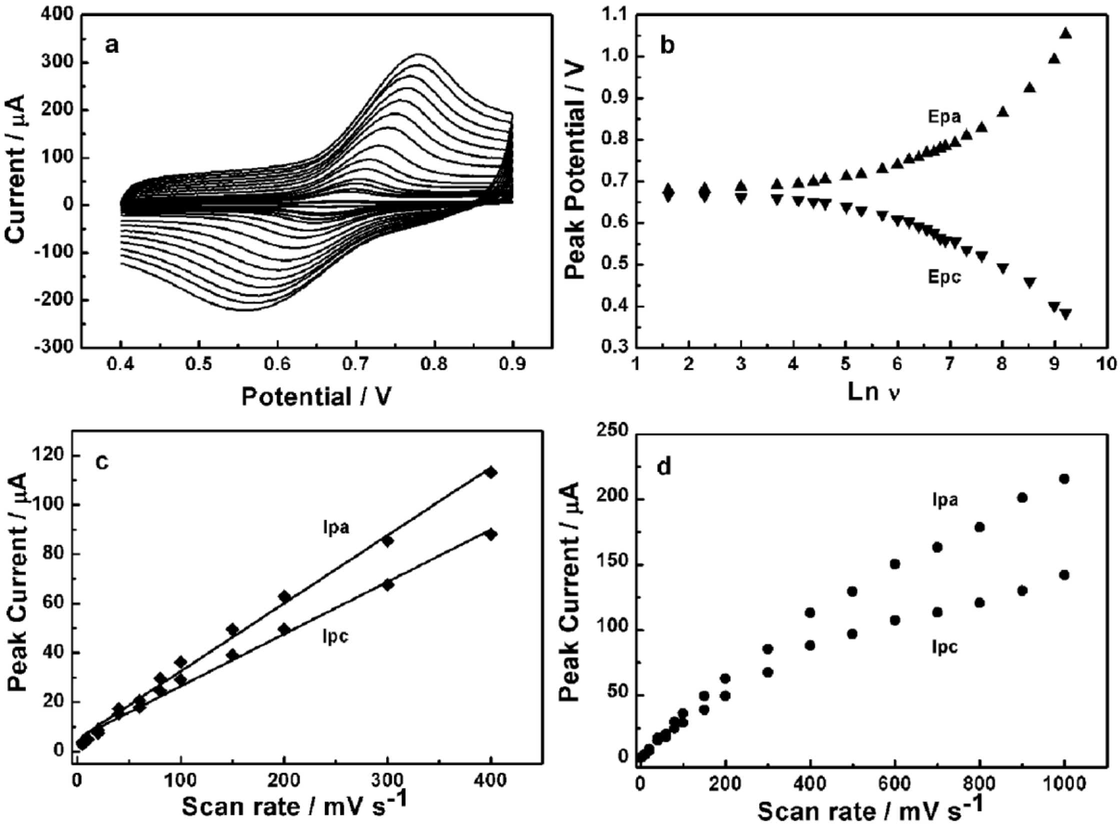

Fig. 7 (a) Cyclic voltammograms of SY in 0.1 M pH 7.0 BR at different scan rates. Scan rates (from inner to outer): 5, 10, 20, 40, 60, 80, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mV s^{-1}. (b) Various of peak potentials vs. the logarithm of the scan rates (5-10000 mV s^{-1}). (c) The plot of cathodic and anodic peak currents vs. scan rates (5-400 mVs^{-1}). (d) The plot of cathodic and anodic peak currents vs. scan rates (5-1000 mV s^{-1}).

3.4 Determination of SY

The quantitative analysis of SY was investigated by SWV method for this method can provide better peak resolution and higher current sensitivity. Fig. 8a shows SWV curves of different concentrations of SY on pyy-SCNT/GCE. The oxidation peak current (Ipa) was linearly proportional to the concentration of SY in the range of 2.0×10^{-9} to 1.5×10^{-6} M and the corresponding regression equation can be expressed as I_{pa} (μA) = 91.53 C (μM) + 1.00 (R^2=0.996). Compared with SCNT (slope: 19.09, Fig. 8b, line b), ppy spheres (slope: 0.60, Fig. 8b, line c), the slope of the calibration plot in the present work is much higher, and the detection limit of the present modified electrode is much lower (3.0×10^{-10} M, S/N=3). The result of ppy-SCNT composites modified GCE detection platform is compared with other published results in Table 1. It is obvious that the prepared electrode possess the highest sensitivity (91.53 μA/μM) toward the determination of SY.

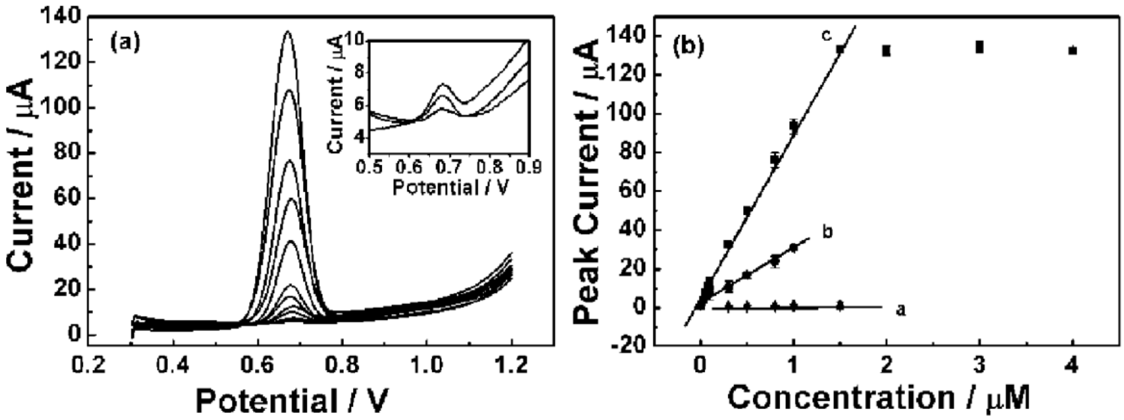

Fig. 8 (a) The SWVs of increasing SY concentration in 0.1 M BR (pH 7.0), SY concentration was 0.002, 0.005, 0.01, 0.03, 0.05, 0.08, 0.1, 0.3, 0.5, 0.8, 0.8, 1.0 and 1.5 μM (from bottom to top), respectively. Right inset: SWVs of SY in low concentration: 0.002, 0.005 and 0.01 μM. (b) The calibration curve of SY obtained with (a) bare GCE, (b) SCNT/GCE, (c) ppy-SCNT/GCE.

3.5 Stability, Reproducibility, and Interferences

The long-term stability of the modified electrode was evaluated through the SWV response of 0.5 μM SY. When the ppy-SCNT/GCE was not in use, it was stored at 298 K. 82.0% of the initial response of the ppy-SCNT/GCE for SY was remained after 21 days when using once per 3 days, suggesting favorable stability of the ppy-SCNT/GCE. The reusability and reproducibility of ppy-SCNT modified GCE was also investigated. Five different modified electrodes were also used to measure 0.5 μM SY with SWV method, the SWV current response remained almost constant and the relative standard deviation (RSD) was 3.01% proving good reproducibility of ppy-SCNT modified electrode. Before or after every measurement, the electrode can be regenerated by cycling voltammetric from 0.3 V to 1.0 V in 0.1 M pH 7.0 BR solution for 20 times, implying excellent repeatability.

The interferences of many foreign species for the determination of SY were studied. The response of the ppy-SCNT modified electrode to 0.5 μM SY was not affected by additions of 100-fold glucose, glycine, cysteine, citric acid,

Table 1 Comparisons of different electrodes in the determination of SY.

Electrodes	Linear range (nM)	Detection limit (nM)	Sensitivity (μA/μM)	Ref.
Alumina microfibers/CPE[a]	0.5-100	0.16	26.19	16
EGPE[b]	50-2000	5	48.02	19
SMDE[c]	11-200	11	--	20
ATP[d]/EGPE	2.5-1500	1	74.56	21
Poly-L-cys[e]/GCE	8-700	4	24.262	15
Ppy-SCNT/GCE	2-1500	0.3	91.53	This work

[a] Carbon paste electrode.
[b] Expanded graphite paste electrode.
[c] Static mercury drop electrode.
[d] Attapulgite.
[e] Poly (L-cysteine).

sodium oxalate and vitamin C. Otherwise, some ions such as 500-fold concentration of SO_4^{2+}, NO_3^-, Cl^-, Mg^{2+}, Ca^{2+}, Na^+ and K^+, had no influence on the modified electrode for the detection of 0.5 μM SY. The interference of other yellow dyes like Tartrazine was also studied. It was found that the sensor possess good selectivity even if the SY and Tartrazine are added simultaneously to the same food. The square wave voltammogram of one kind of soft drink sample in 0.1 M pH 7.0 BR buffer solutions after 5-min accumulation was depicted in Fig. 9a. During the potential sweep from 0.3 to 1.2 V, two oxidation peaks (O_1 and O_2) appear at the ppy-SCNT/GCE. After different amounts of SY standard solutions were added into, the square wave voltammogram were then recorded in Fig. 9b-g. From the comparison of curves (a) and (b-g), it was found that the oxidation peak current of O_1 increased while the oxidation peak current of O_2 unchanged, indicating the correspondence of O_1 to SY. And it has been demonstrated that the O_2 was correspondence to Tartrazine based on the square wave voltammogram of Tartrazine standard solution (not shown). Obviously, the existence of Tartrazine didn't influence the determination of SY with the sensor.

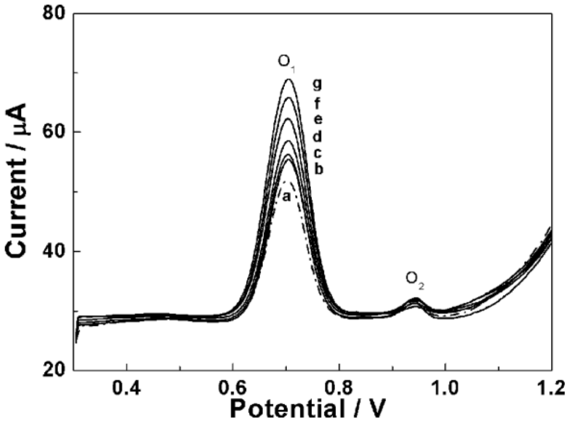

Fig. 9 SWVs of a soft drink sample (curve a) and (a) + different concentrations of SY standard solution (curve b-g) at ppy-SCNT/GCE.

3.6 Practical Application

To test the practicality of the proposed approach, the concentration of jelly (brands of Strong, China) and two kinds of fruit drink (Fanta and Mirinda) purchased from a local market was detected with this method. Proper amount of jelly was crumbled and collected in a beaker, followed by extracting ultrasonically by 25 mL water for 20 min for three times, and the resulting extraction was gathered and diluted with water to 50 mL and filtered through a 0.45 μm membrane filter. The fruit drink sample was filtered through a 0.45 μm membrane filter without else pretreatment. Upon 1.0 mL of drink sample was added into 20 mL 0.1 M BR buffers, SWV curves were recorded from 0.3 to 1.0 V after 5-min accumulation. The content was determined by standard addition method, and the results are listed in Table 2. Each sample solution undergoes three parallel detections and the RSD were below 5%, suggesting that the results obtained by ppy-SCNT modified electrode are acceptable. And the recoveries for orange-flavored sports drink were changed between 98.7% and 100.3%. Therefore, the fabricated electrode for the determination of SY is accurate and feasible.

Table 2. Determination of SY in food samples using ppy-SCNT/GCE.

Sample	Spiked (mg L^{-1})	Expected (mg L^{-1})	Found (mg L^{-1})[m]	Recovery
Jelly	-	-	2.69 ±0.22	-
	0.14	2.83	2.79 ±0.19	98.6%
Fruit drink 1 (Fanta)	-	-	2.10 ±0.92	-
	0.23	2.33	2.34 ±0.60	100.5%
Fruit drink 2 (Mirinda)	-	-	2.99 ±0.92	-
	0.45	3.44	3.46 ±0.60	100.5%

[m] Values reported are mean of three replicates.

4 Conclusion

In this study, the ppy-SCNT composites were successfully prepared via a facile situ chemical oxidative polymerization process at room temperature. The ppy could prevent the aggregation of SCNT via π-π interaction. And the composite modified electrode owns larger effective surface area. The electrochemical test results show that the ppy-SCNT composites modified electrode exhibits excellent sensitivity for Sunset yellow. Moreover, this electrochemical sensor was suitable for building a broader application of various types of azo dyes (such as Amaranth and Tratarzine) and easy to achieve, which might offers an alternative strategy for the on-site monitoring of other hazard components in food.

Acknowledgement

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