Cyclic voltammetric determination of capsaicin by using electrochemically deposited tin and reduced graphene oxide on screen-printed carbon electrodes

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ABSTRACT: Tin and reduced graphene oxide (Sn/rGO) was prepared by an electrochemical deposition and modified on a screen-printed carbon electrode (SPCE) in order to improve the electrode selectivity and sensitivity for determination of capsaicin in real samples. The modified electrode was characterized for its surface morphology by scanning electron microscopy (SEM). An elemental analysis of prepared catalysts was confirmed by energy dispersive spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). The experimental conditions influencing determination of capsaicin were optimized. The experiment was carried out in a sodium acetate buffer solution pH 3.0 at a scan rate of 50 mV/s. The Sn/rGO/SPCE showed a linear working range of 0.2–22 µM of capsaicin concentrations. The limit of detection and limit of quantification were 0.005 µM (S/N=3) and 0.02 µM (S/N=10), respectively. The prepared electrode was successfully applied to determine capsaicin in real chili samples and chili sauces.

KEYWORDS: capsaicin detection, modified electrode, electrocatalyst, electrochemical sensor

INTRODUCTION

Chili is one of the most popular ingredients in food owing to its unique characteristics for desirable taste and improving appetite [1]. The spiciness and pungency of chili pepper is attributed to a compound group known as "capsaicinoids", which are found in members of the capsicum family [2, 3]. Capsaicin ($C_{18}H_{27}NO_3$) is a main compound in the capsaicinoid group that includes dihydrocapsaicin, homocapsaicin and homodihydrocapsaicin [4–6]. Capsaicin has been widely used in pharmaceutical and medical applications due to its remarkable properties, such as boosting metabolism to increase amount of heat in body and burn more calories [7], reducing blood pressure [8], helping dilation of blood vessel [9], and improving blood circulation [10]. Capsaicin also has antioxidative [11], antibacterial [12] and anticarcinogenic [13] properties.

Due to the importance of capsaicin in culinary and biomedical uses, a simple, rapid and accurate determination of capsaicin is necessary, particularly in food and pharmaceutical industries. Several analytical techniques for determination of capsaicin, such as spectrophotometry, gas chromatography (GC) [14], high performance liquid chromatography (HPLC) [6], gas chromatography-mass spectrometry (GC-MS) [15], and liquid chromatography-mass spectrometry (LC-MS) [16], have been reported. However, these methods require the use of expensive instruments with complicated procedure and long response time. Alternate approach for capsaicin determination could be done via electrochemistry due to its advantages, such as high efficiency, good reproducibility, greater linear response range, and easy operation. Among electrochemical techniques, cyclic voltammetry is the most widely used to study the electrochemical behavior of electroactive species by using biosensor [17, 18] or non-biosensor [19].

Electrochemical determination of capsaicin was firstly reported by Kachoosangi et al [20] by using adsorptive stripping voltammetry at a carbon nanotube (CNT) based electrochemical sensors. Other approaches were reported on different types of electrodes for detection of capsaicin, such as boron-doped diamond electrode [21], glassy carbon electrode [22], carbon nanotube (CNT) [19], graphene oxide (GO) [23], reduced graphene oxide (rGO) [24], precious metal [25, 26], non-precious metals [23], carbon paste electrode modified with amino-functionalized mesoporous silica [27], and

screen printed single-walled CNT [19]. Furthermore, several metallic nanoparticles modified electrode surface and their enhanced sensitivity and selectivity were also investigated, for example, Ag/Ag$_2$O functionalized reduced graphene oxide (rGO) on screen-printed electrode (SPE) [25] and ruthenium nanoparticles decorated CNTs [28]. The precious metals always show high catalytic activity; however, the obtained electrodes have a high cost of production. The complicated and expensive electrode fabrication process may restrict the improving of capsaicin sensor in the future. Hence, a disposable, cheap, sensitive, and selective electroanalytical sensor for determination of capsaicin is necessary.

The screen-printed carbon electrode (SPCE) is a low cost sensor. It can be modified and tailored to appropriately serve the demand of the end user and offer high potential for commercial applications. As the sensitivity and selectivity of the SPCE towards the target molecules are imperative, the reduced graphene oxide (rGO), a derivative of graphene, has attracted tremendous attentions due to its properties, such as high surface area and excellent electrochemical properties. However, the limited conductivity of the rGO and its poor dispersibility are still challenging factors for the rGO modified electrode. In order to solve these problems, rGO has been functionalized with precious metals [25, 26] and non-precious metals [22]. Tin (Sn) is a p-block metal that has been widely used for promoting adsorption of several molecules on an electrode surface [29, 30]. Tin can supply highly oxophilic sites where one oxygen atom in the target molecule can be adsorbed on the electrode surface. It is possible for tin to form a key part of active site, either purely as a coordination site or indeed as part of the redox system. Furthermore, tin has been used as a catalyst due to its high selectivity and performance to facilitate electron transfer between electroactive species and electrode surface [31, 32].

Based on the facts mentioned above, we aimed to develop disposable electrochemical sensors by using non precious metal, rGO and SPCE. Therefore, Sn and rGO were employed to enhance electrocatalytic activity of SPCE for determination of capsaicin in our present work. The Sn/rGO/SPCE was prepared by using electrochemical deposition. Investigation of capsaicin adsorption on the newly modified electrode was then achieved by cyclic voltammetry. The electrode was subsequently used for determination of capsaicin in Bird's eye chili, Karen chili and chilli sauces.

MATERIALS AND METHODS

Reagents

Capsaicin (C$_{18}$H$_{27}$NO$_3$) with ⩾99% purity, tin (II) chloride dihydrate (SnCl$_2 \cdot$2H$_2$O) with ⩾99.995% purity and graphene oxide (2 mg/ml dispersion in H$_2$O) were obtained from Sigma-Aldrich (St. Louis, USA). Standard tested interfering substances, such as D-(+)-glucose, D-(-)-fructose with ⩾99% purity, zinc (II) chloride anhydrous with ⩾97% purity, copper (II) chloride were also obtained from Sigma-Aldrich (St. Louis, USA). Potassium chloride and sodium hydroxide anhydrous pellets were purchased from Carlo Erba Reagents (Barcelona, Spain). The electrolyte solution was a mixture of glacial acetic acid and anhydrous sodium acetate obtained from Carlo Erba reagents (Barcelona, Spain) and Sigma-Aldrich (St. Louis, USA), respectively. Carbon paste and Ag/AgCl paste were purchased from SunChemical (Torfaen, UK).

Preparation of tin and reduced graphene oxide screen-printed carbon electrode (Sn/rGO/SPCE)

A screen-printed technique was applied for making electrodes on a chip for electrochemical measurement. Carbon paste was screen-printed onto a 10 mm × 25 mm of polyvinyl chloride (PVC) sheet (Paper Thai Co., Ltd.) and dried at 60 °C for 30 min to form a working electrode area of 3 mm diameter and a counter electrode. After that, Ag/AgCl paste was applied onto the pre-screened PVC to form a reference electrode and dried at 60 °C overnight. An insulating ink was finally screen-printed onto three electrodes to exclude the detection area. The printed carbon electrode was dried at room temperature and kept in a desiccator.

A mixture of 0.5 ml GO, 103 µl of 0.05 mM tin (II) chloride solution and 1.4 ml deionized water was sonicated for 1 h to prepare tin and graphene oxide (Sn/GO) catalyst ink. A 6 µl Sn/GO catalyst ink was drop-casted on the working electrode of the bare SPCE and dried at room temperature. A 100 µl sodium acetate buffer solution was dropped to cover all modified SPCE surface, and the electrode was subjected to chronoamperometry with an applied potential of −0.44 V for 5 min to obtain a Sn/rGO/SPCE. To obtain optimum potential and time for Sn electrodeposition, the potentials and time were varied, as shown in Fig. S1 in supplementary data. The potential of −0.44 V and the deposition time for 300 s showed the maximum peak current. The potential of electrode was controlled by the Autolab PGstat20 potentiostat (Metrohm-Autolab,

Netherlands).

Electrochemical measurement

A 0.00764 g of capsaicin powder was dissolved in 250 ml sodium acetate buffer solution (pH 3.0) to obtain 100 μM capsaicin stock solution. The stock solution was then diluted with sodium acetate buffer solution (pH 3.0) to obtain capsaicin standard solutions in a concentration range of 0.2–22 μM. For the the study of capsaicin determination, the cyclic voltammetric (CV) measurement was conducted over the range from 0 to 1.0 V at a scan rate of 50 mV/s in 100 μl of 0.01 M sodium acetate buffer solution (pH 3.0) to check the performance of the electrode. The sodium acetate buffer solution was removed. A 100 μl of the capsaicin standard solution was then dropped on the electrode surface for the determination of capsaicin at a scan rate of 50 mV/s.
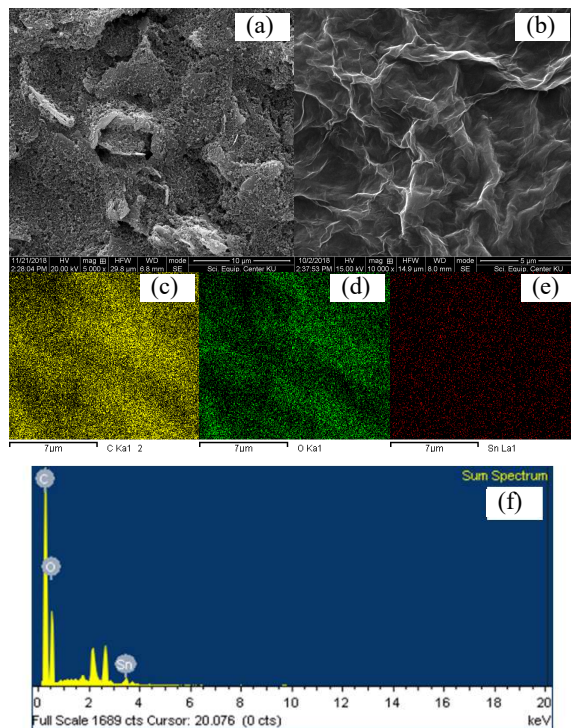
Preparation of real samples

The as-prepared Sn/rGO/SPEC electrode was used to test the electrochemical determination of capsaicin in real samples. Bird's eye chilli, Karen chili and chili sauces were obtained from a local market in Bangkok. The extraction of capsaicin from the real samples was carried out following procedure of Ya et al [27]. A 0.2 g ground sample was mixed with 25 ml ethanol, then sonicated for 1 h, centrifuged at 12 000 rpm for 20 min, and filtered. The supernatant was diluted with sodium acetate buffer solution (pH 3.0) to obtain 50 ml stock solution of chili samples.

A standard addition method was adopted to measure capsaicin in real samples. A 100 μM of capsaicin standard solution was spiked into the stock solution of chili samples to give the concentration of 5, 10, 15, and 20 μM in 0.01 M sodium acetate buffer solution (pH 3.0). The CV measurements of spiked and non-spiked samples were carried out under the optimum condition at 50 mV/s. The obtained results were calculated for the percentage recovery (%R) as follows:

$$\%R = \frac{C_S - C_U}{C_A} \times 100$$

where C_S = concentration of capsaicin in spiked sample, C_U = concentration of capsaicin in unspiked sample and C_A = concentration of capsaicin added in the unspiked sample. Calibration curves in the range of 0.2–22 μM were used for the calculation of capsaicin concentrations in the chili samples.
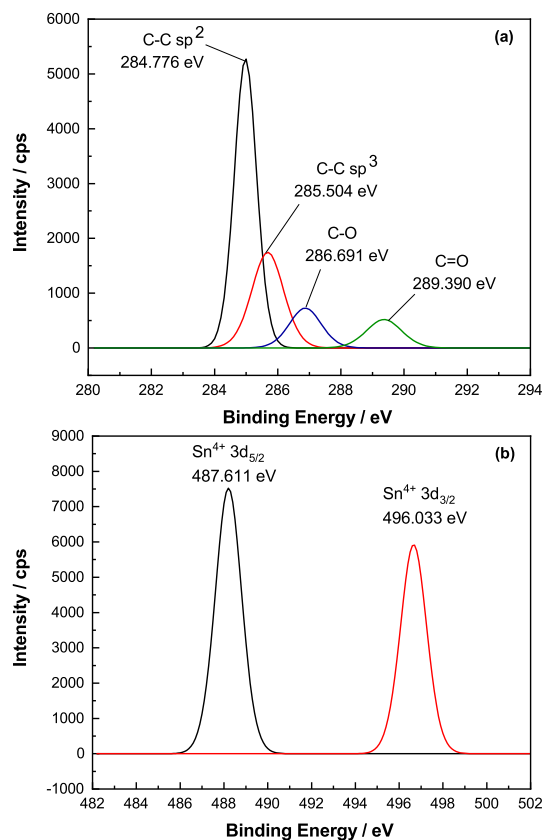

Fig. 1 SEM images of (a) bare SPCE and (b) Sn/rGO/SPCE with elemental mapping of (c) carbon, (d) oxygen, (e) tin, and (f) EDS spectra of Sn/rGO/SPCE.

The experiment was repeated three times for each concentration and the relative standard deviation (RSD) was calculated.

RESULTS AND DISCUSSION

Characterization of Sn/rGO/SPCE

SEM images of bare SPCE and Sn/rGO/SPCE are shown in Fig. 1a and Fig. 1b, respectively. A distinct difference in the surface morphology was observed between the bare SPCE and the Sn/rGO/SPCE. The bare SPCE showed roughness of carbon sheet, while the Sn/rGO/SPCE showed a cloudy and wrinkled texture of rGO sheets that fully covered on the SPCE surface. The spherical-shaped particles of Sn were however not observed on the rGO sheets because they were smaller than the resolution limitation of the instrument and possibly under rGO sheets. Fig. 1(c,d,e) show a composition of Sn/rGO by elemental mapping of carbon, oxygen and tin, respectively. The EDS analysis of Sn/rGO/SPCE gave the spectra of carbon and oxygen at 0.27 and 0.52 keV [33] (Fig. 1f), confirming the elemental composition of rGO. Although, no Sn particle presented in the SEM image, a signal of Sn at 3.44 keV
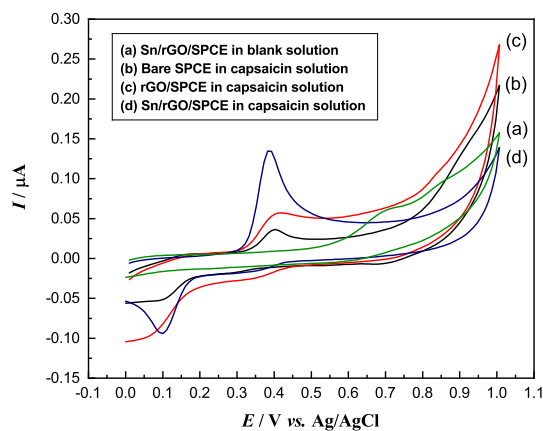
Fig. 2 High resolution XPS spectra of (a) C 1s and (b) Sn 3d of Sn/rGO/SPCE.

was observed. This could be a confirmation for the presence of Sn in the modified Sn/rGO/SPCE electrode [34].

Surface composition and electronic valence states of the Sn/rGO/SPCE were confirmed by using XPS technique. Fig. 2a shows the C 1s spectrum at 284.7 eV, which indicates the formation of C—C sp^2. In addition, the spectra of C 1s were deconvoluted into three peaks of C—C sp^3 at 285.5 eV, C—O at 286.7 eV and C=O at 289.4 eV [34, 35]. The Sn 3d spectrum in Fig. 2b shows two de-convoluted peaks of which the binding energy at 487.6 eV and 496.0 eV, corresponding to the Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ of Sn$^{2+/4+}$ [36]. No doublet due to metallic Sn (493.2 and 484.8 eV) was observed, suggesting that Sn is easily oxidized at room temperature [37, 38].
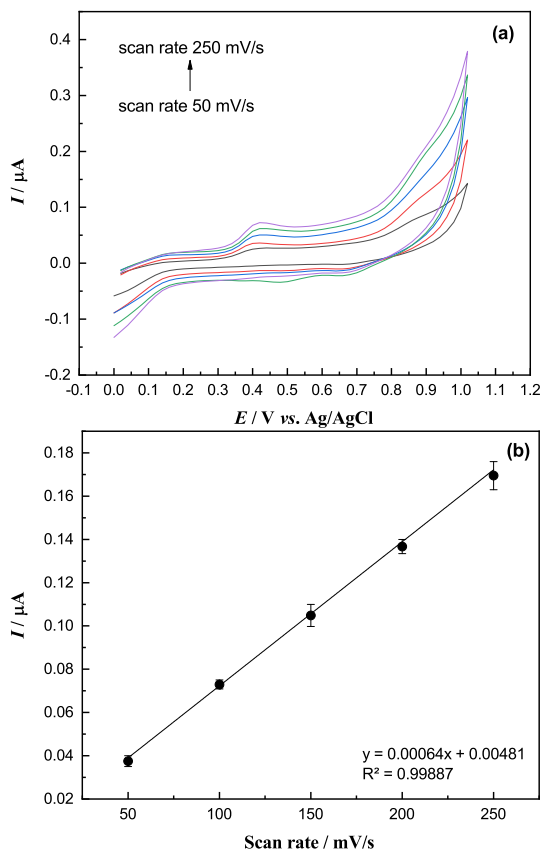
Electrochemical behavior of Sn/rGO/SPCE on capsaicin determination

To study the electrochemical performance of the prepared SPCE, CV measurement was used to determine capsaicin in sodium acetate buffer solution.

Fig. 3 Cyclic voltammograms in 0.01 M sodium acetate buffer solution (pH 3.0) of (a) Sn/rGO/SPCE, in 2 μM capsaicin and sodium acetate buffer solution (pH 3.0) of (b) bare SPCE, (c) rGO/SPCE and (d) Sn/SPCE/rGO at 50 mV/s.

Fig. 3 shows the cyclic voltammograms of the Sn/rGO/SPCE in a blank 0.01 M sodium acetate buffer solution, the bare SPCE, the rGO/SPCE and the Sn/rGO/SPCE in 2 μM capsaicin solution at the scan rate of 50 mV/s. The cyclic voltammogram signal of the Sn/rGO/SPCE obtained in 0.01 M sodium acetate buffer solution (pH 3.0) showed a peak at $E_{pa} = +0.70$ V, which was attributed to tin oxide formation. Compared with the Sn/rGO/SPCE in blank solution, the SPCE, the rGO/SPCE and the Sn/rGO/SPCE in 2 μM capsaicin solution showed the oxidation peak at $E_{pa} = +0.40$ V on the forward scan, which was capsaicin oxidation. However, the $E_{pa} = +0.70$ V was discernible in a presence of capsaicin since the adsorption of capsaicin on the catalyst surface suppressed the presence of this anodic peak. The backward scan demonstrated the peak at $E_{pc} = +0.10$ V, which was the reduction of *O*-benzoquinone. The position of the cathodic peak was however far from that of anodic peak, suggesting a sluggish reduction process. An oxidation peak and another pair of redox peaks related to the capsaicin reactions at the surface of the bare SPCE and the Sn/rGO/SPCE are shown, which are in accordance with the mechanism in Fig. 5. This mechanism was proposed in the previous report [18]. The electrochemical oxidation of capsaicinoids is an irreversible step. It involves the oxidation of phenolic hydroxyl group and the hydrolysis of the methoxy group, resulting in the production of an *O*-benzoquinone unit [20, 21]. The oxidative peak at +0.40 V showed the highest sensitivity compared
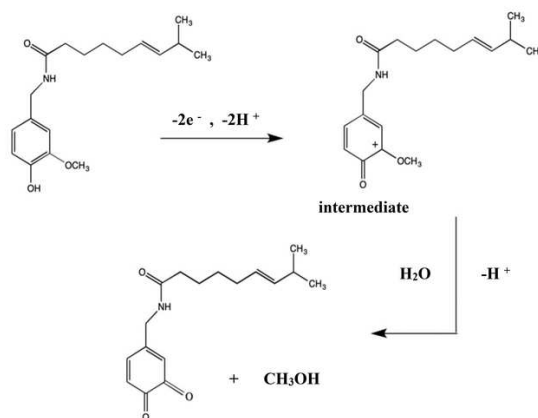
Fig. 4 (a) Cyclic voltammograms of Sn/rGO/SPCE and (b) linear plot for anodic peak of Sn/rGO/SPCE in 2 μM capsaicin and sodium acetate buffer solution (pH 3.0) at difference scan rates from 50 to 250 mV/s.

with the cathodic peak. It was then selected to quantify capsaicin in chilli samples. The anodic peak current of capsaicin on the Sn/rGO/SPCE was significantly higher than those on the rGO/SPCE and the bare SPCE, indicating that the presence of Sn can enhance the sensitivity of the electrode. The catalytic performance of the Sn/rGO/SPCE was possibly attributed to the uniform distribution of Sn over rGO sheet, which resulted in the active site on the prepared SPCE. Furthermore, the presence of Sn on the SPCE surface increased the adsorption of capsaicin and facilitated the electron transfer in capsaicin oxidation. Therefore, the Sn/rGO modified SPCE electrochemical sensor could be potentially used for the detection of capsaicin.

Effect of scan rate on capsaicin determination

Electrochemical behaviors of capsaicin were investigated at different scan rates, as shown in Fig. 4. The cyclic voltammograms of the Sn/rGO/SPCE for
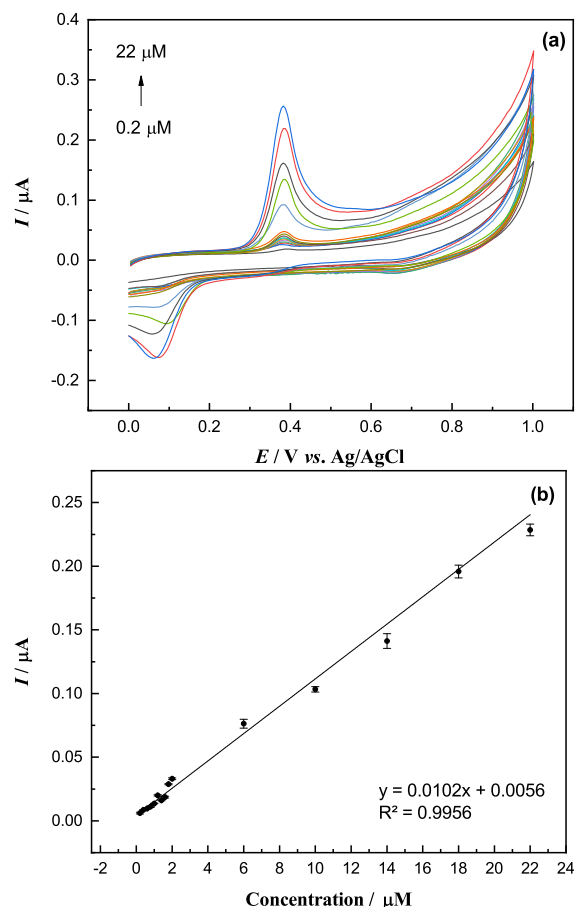

Fig. 5 Mechanism of the electrochemical oxidation of capsaicin [20].

2 μM capsaicin in sodium acetate buffer solution (pH 3.0) were determined at different scan rates, ranging from 50 to 250 mV/s. The effect of scan rate on peak potential of capsaicin oxidation was investigated. The anodic peak potential positively shifted as the scan rate increased (Fig. 4a). The anodic currents of capsaicin improved with increasing scan rate. A good linear relationship between the peak current and the scan rate was obtained with a regression equation of $I_{\mathrm{pa}} = 0.00064v + 0.00481$ ($R^2 = 0.998$) (Fig. 4b). It was apparent that the anodic peak currents were linear with the scan rates, indicating that the electrochemical oxidation of capsaicin on the Sn/rGO/SPCE was an adsorption controlled process.

Effect of pH on capsaicin determination

A study of pH affecting the capsaicin oxidation in the pH range of 1.0–6.0 in sodium acetate buffer solution demonstrated that the anodic peak currents of capsaicin increased with rising pH and reached the maximum at pH 3.0, and dropped afterwards, as shown in Fig. S2. The pH of electrolyte solution clearly affected anodic currents due to hydrolysis of 2-methoxy group in capsaicin molecule, as shown in the mechanism in Fig. 5 [20]. At pH > 3.0 the *O*-methoxyphenol moiety of capsaicin was partially deprotonated, resulting in inefficient accumulation of capsaicin on the Sn/rGO/SPCE [20]. At the pH lower than 3.0, the peak currents dramatically decreased, since high amounts of protons in the acidic solution adsorbed on the tin oxide, resulting in less amount of capsaicin on the surface of the Sn/rGO/SPCE. Thus, the sodium acetate buffer so-

Fig. 6 (a) Cyclic voltammograms and (b) linear plots between concentration of capsaicin and anodic peak current in 0.2–22 µM capsaicin and sodium acetate buffer solution (pH 3.0) at 50 mV/s.

Table 1 Comparison of efficiency of Sn/rGO/SPCE with literature of modified electrodes for capsaicin determination.

Modified electrode	LOD (µM)	Linear range (µM)	Ref.
PDDA-rGO/Pd modified GCE	0.10	0.32–64	[29]
MCFs modified CPE	0.08	0.76–11.65	[39]
Ag/Ag$_2$O-PSS-rGO modified SPE	0.40	1.0–60	[28]
MWCNT modified BPPGE	0.31	0.5–60	[20]
Sn/rGO modified SPCE (this work)	0.005	0.2–22	

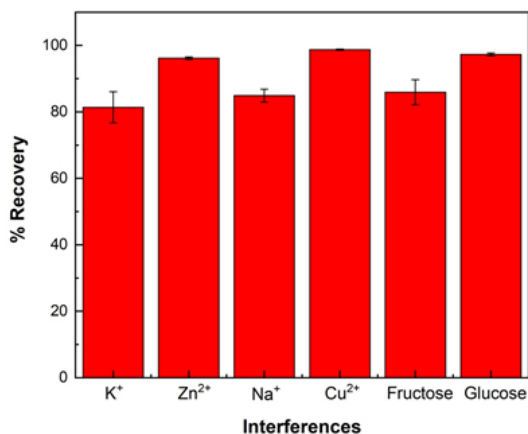lution pH 3.0 was chosen as the optimized value for capsaicin detection.

Electrochemical determination of capsaicin

A relationship between the anodic peak current and concentration of capsaicin was investigated by using cyclic voltammetry under the optimal conditions. Fig. 6a shows cyclic voltammograms obtained from different concentrations of standard capsaicin solution ranging from 0.2 µM to 22 µM. The anodic and cathodic peak currents were presented at +0.40 V and +0.10 V on the forward and backward scans, respectively. At a potential of +0.40 V, the anodic peak currents increased as a function of capsaicin concentrations. Fig. 6b shows a linear calibration plot of the capsaicin concentrations and the anodic peak currents measured by using the Sn/rGO/SPCE, giving a regression equation of I_{pa} (µA) = 0.0102 C (µM) + 0.0056 with R^2 = 0.9956. The limit of detection (LOD) and the limit of quantification (LOQ) were estimated at 0.005 µM (S/N=3) and 0.02 µM (S/N=10), respectively. It was noticed that the precision represented by the error bar of each standard solution was remarkably good, ranging between 1.29% RSD and 4.50% RSD of the lowest concentration in the range. A comparison of the Sn/rGO/SPCE efficiency with those of other modified electrodes was given in Table 1. The Sn/rGO/SPCE showed lower LOD and a linear range comparing to the previously purposed electrodes. These results were due to the oxophilicity of tin and its favourable interaction with capsaicin on the surface of Sn/rGO/SPCE. Therefore, tin increased the adsorption of capsaicin on the electrode surface along with its catalytic activity. Furthermore, the dispersion of tin on the rGO can increase surface area and active sites of the catalyst, proving an excellent quantitative performance for sensitive and rapid capsaicin determination by using the proposed Sn/rGO/SPCE. However, the mechanism of the capsaicin oxidation was similar to the mechanism in Fig. 5 proposed in the previous report [20].

Electrochemical determination of interference

Chili and its food products usually contain additives and chemical substances, such as K$^+$, Zn^{2+}, Na$^+$, Cu^{2+}, glucose and fructose [32]. These compounds can possibly disturb the electrooxidation of capsaicin. Therefore, the selectivity and sensitivity of the Sn/rGO/SPCE were evaluated for potential interferences for the analysis [40]. In a 130 µM capsaicin standard solution, 2 mM interfering species each in sodium acetate buffer solution (pH 3.0) was added. % Recovery of between 81%–97% was obtained, as shown in Fig. 7, proving that the interfering species did not have any influence on the capsaicin determination, and the Sn/rGO/SPCE was very selective to capsaicin. The prepared electrode was therefore suitable for quantitative determination of capsaicin.

Fig. 7 Comparisons of 2 mM interfering substances added into 130 μM capsaicin in sodium acetate buffer solution (pH 3.0) under the optimized conditions of measurement using the Sn/rGO/SPCE.

Reproducibility and stability of Sn/rGO/SPCE

To confirm the precision of the proposed electrode, the reproducibility and stability of Sn/rGO/SPCE were examined. Three electrodes prepared by the same procedure were used to determine 2 μM and 22 μM capsaicin in acetate buffer solution (pH 3.0). The relative standard deviation (RSD) for the anodic peak currents of 2 μM and 22 μM capsaicin were approximately 1.89% and 2.01%, respectively, suggesting high reproducibility of the Sn/rGO/SPCE. In addition, the stability of the electrode was evaluated by measuring the anodic peak current of 22 μM capsaicin over a one week period. It was observed that the Sn/rGO did not come off during measurement, assuring that the catalyst ink of Sn/rGO was well-adhered to the surface of SPCE. The electrode was stored in a desiccator over the testing period. The anodic peak current of 22 μM capsaicin in an acetate buffer solution (pH 3.0) decreased by 8.90% at the end of the week, indicating a high stability of the electrode. The intra-day measurement was carried out with three independent determinations of 10 μM capsaicin in acetate buffer solution (pH 3.0), resulting in an excellent RSD of 2.02%. Furthermore, the inter-day precision obtained by measuring anodic peak current for three consecutive days in 10 μM capsaicin solution was satisfactorily achieved at 2.58% RSD.

Electrochemical analysis of real samples

Capsaicin in real samples, such as Karen chili, Bird's eye chili and chili sauces was also successfully determined by using the Sn/rGO/SPCE. Measurement results of spiked and non-spiked samples are shown in Table 2. The results for capsaicin determination in real samples of Karen chili, Bird's eye chili and chili sauces A and B were satisfactory with the recovery of 107.26, 104.25, 94.05 and 94.10%, respectively. Triplicate analyses of the samples were achieved with the reasonably good RSDs, 3.62%–7.66%. The concentration in μM has been converted to ppm, and to Scoville units. A 1 ppm is approximately equal to 15 Scoville units. The results confirmed a potential application of the Sn/rGO/SPCE for determination of capsaicin in chili samples.

CONCLUSION

In the present work, the remarkable analytical sensitivity of the Sn/rGO/SPCE, together with its simple preparation and economical cost, makes such the thin-film electrode having a great potential application as a capsaicin sensor for testing the heat in commercial food products. The oxidation of capsaicin produced derivatives that possibly adsorbed on the electrode surface, resulting in the loss of electrode performance during repeated experiment with the same electrode. The further advantage of the Sn/rGO/SPCE was hence its single-use, which eliminated the fouling problem of the electrode surface. In the extraction step of capsaicin from chili samples, some potential interfering species could be co-extracted; however, the dilution of high concentrated capsaicin extract with buffer was needed for detection at low concentration range. Any interfering species were, therefore, subsequently reduced during the measurement. These features clearly show that the proposed thin electrode successfully performed as the effective capsaicin electrochemical sensor for food and pharmaceuticals at a very low-cost.

Appendix A. Supplementary data

Supplementary data associated with this article can be found at http://dx.doi.org/10.2306/scienceasia1513-1874.2020.076.

Table 2 Determination of capsaicin in real sample.

Sample	Original value (μM)	Added (μM)	Found (μM)	% Recovery	Capsaicin (μg/ml)	Scoville unit
Karen chili	4.68	4.94	9.96	107.26 ± 4.13	3.04	45.63
Bird's eye chili	4.70	5.16	10.06	104.25 ± 4.04	3.07	46.09
Chili sauce A[a]	12.26	12.04	23.57	94.05 ± 3.55	7.20	107.98
Chili sauce B[a]	12.03	11.57	22.89	94.10 ± 7.60	6.99	104.86

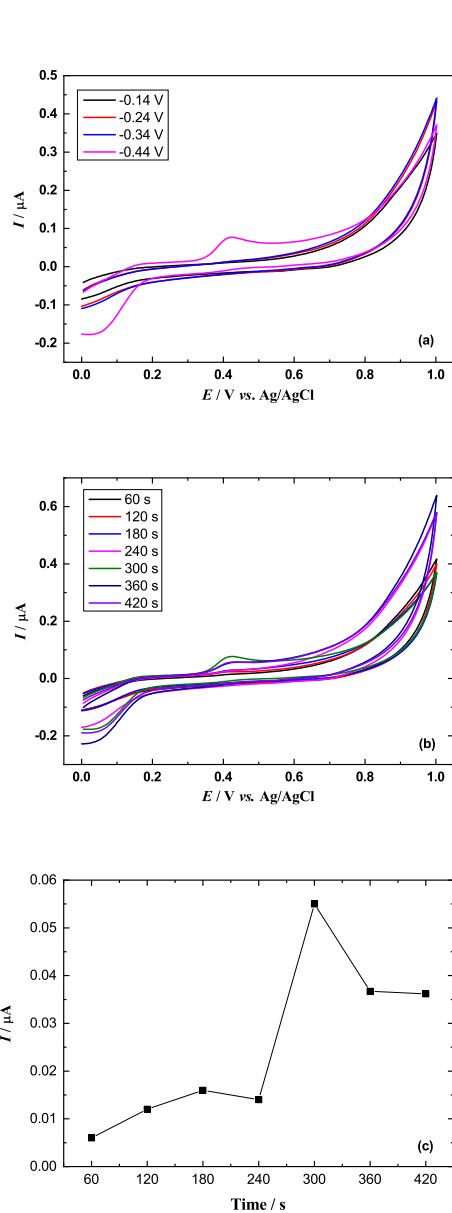[a] A and B represented different manufacturers.

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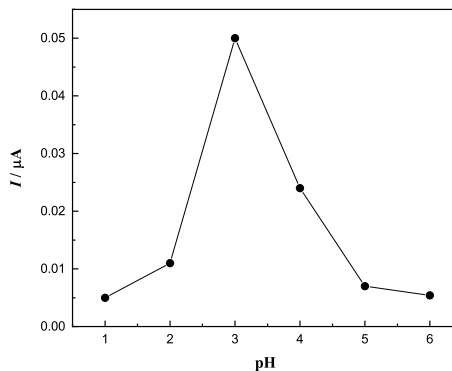
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Appendix A. Supplementary data

Fig. S2 Plot between anodic peak current of the Sn/rGO/SPCE in 2 mM capsaicin and sodium acetate buffer solutions with different pH from 1.0 to 6.0 at 50 mV/s.

Fig. S1 (a) Cyclic voltammograms of different Sn electrodeposition potentials, (b) cyclic voltammograms of different Sn electrodeposition time, and (c) linear plots between time anodic peak current in 2 mM capsaicin and sodium acetate buffer solution (pH 3.0) at 50 mV/s.