Amplified electrochemical determination of maltol in food based on graphene oxide–wrapped tin oxide@carbon nanospheres

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Abstract

The study presents a new approach for rapid and ultrasensitive detection of maltol using a glassy carbon electrode (GCE) modified with graphene oxide–wrapped tin oxide@carbon nanospheres (SnO₂@C@GO). The morphological and components properties of SnO₂@C@GO nanocomposites were investigated by means of X-ray diffraction spectroscopy, Raman spectroscopy, field emission scanning electron microscopy, high resolution transmission electron microscopy, and electrochemical impedance spectroscopy. SnO₂@C@GO nanocomposite on a GCE had a synergetic effect on the electrochemical oxidation of maltol by means of square wave voltammetry. Under the optimum conditions, anodic peak current response of maltol was linear with its concentration in the range of 80 nM~10 μM, and a detection limit of 12 nM was achieved for maltol. The experiment results presented that the method showed good selectivity, sensitivity, reproducibility, and long-term stability, as well as excellent potential for use as an ideal inexpensive voltammetric method applicable

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for complex food matrices.

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Chemical compounds studied in this article

Maltol (PubChem CID: 8369); Tin oxide (PubChem CID: 29011); Carbon (PubChem CID: 5462310); Potassium ferricyanide (PubChem CID: 26250); Glucose (PubChem CID: 5793); Sucrose (PubChem CID: 5988); Glycine (PubChem CID: 750); Citric acid (PubChem CID: 311); Tartaric acid (PubChem CID: 444305); Hydrogen peroxide (PubChem CID: 784); Ascorbic acid (PubChem CID: 54670067); Hydroquinone (PubChem CID: 785)

1. Introduction

Flavor enhancers are important sensory attribute which play important roles in the palatability, taste and acceptability of food, so they are widely used as food additives to enhance the flavor of beverages and foods [Dermiki, Phanphensophon, Mottram, & Methven, 2013]. Therein, maltol (3-hydroxy-2-methyl-4H-pyran-4-one) is a naturally occurring flavor enhancer widely used in food products at levels ranging from 50 to 200 mg kg⁻¹ [LeBlanc & Akers, 1989]. However, maltol has been suspected of having potential harmful consequences on brain, liver, kidney, and spleen functions of the baby when large amount of this enhancer is ingested [Ni, Zhang, & Kokot, 2005]. Considering the adverse effects of maltol, the regulations of the Food and Drug Administration (FDA) and China National Food Safety Standard have forbidden its use in children food and it is not allowed at all in the European Union [Ma, Zhang, Wang, Hou, & He, 2014]. Therefore, the sensitive and convenient analysis of maltol is a potentially important test case in food quality control.

To allow quantitation of maltol at subthreshold concentration, the analytical method has to be highly sensitive, selective, and reliable. Different methods such as gas chromatography–mass spectrometry [Qi & Zhou, 2005], spectrometry [Ni, Wang, & Kokot, 2008], high–performance liquid chromatography [Risner & Kiser, 2008] and two–dimensional liquid chromatography [Avila, Gonzalez, Zougagh, Escarpa, & Rios, 2007] have been reported in the literature, mostly utilizing complex, expensive and time–consuming techniques. Furthermore, many electrochemical methods have previously been developed for the determination of maltol [Chao & Ma, 2014; Ma & Chao, 2014; Ma & Chao, 2013; Zhou, Zhang, Li, Li, & Ye, 2012; Di, Bi, & Zhang, 2004], it can be concluded that the sensing layers of electrode are crucial, so more research is still in process.

As a typical n–type semiconductor, nano–sized tin oxide (SnO_2) including SnO_2 nanosphere has become one of the major focuses semiconducting metal oxides because of the unique electronic, catalytic, and optical properties [Ahn, Kim, Chi, & Kim, 2014; Escuderos, Garcia, Jimenez, & Horrillo, 2013], as well as their simple fabrication, good compatibility, and high natural abundance. And also, SnO_2 based chemical sensors have been investigated. However, such sensors based on SnO_2 usually perform high power consumption and adversely affect the long–term stability, which are still the major challenges for SnO_2 to meet the practical application requirements. Thus, some attempts have been made to overcome these innate shortcomings, by decorating the SnO_2 with thin and intact shells such as carbonaceous materials. We have developed functional carbonaceous materials with conjugative π structure to enhance the electrocatalytic activity of semiconductors [Gan, Shi, Wang, Sun, Lv, & Liu, 2016; Gan, Shi, Hu, Sun, Wang, & Liu, 2015; Huang et al., 2013]. In particular, it has been demonstrated successfully by different groups including ours

that growing a layer of carbon on the surface of metal oxides improves their electrochemical properties. For example, the study of Liu et al showed that the conductive carbon layer endowed the SnO₂-based anode with improved specific capacity and cycling stability, making it more promising for use in lithium ion batteries [Liu, Dou, Ruan, Sun, Chou, & Dou, 2016]. Qu et al found the carbon crystallite on SnO₂ grain boundary could improve the sensitivity and selectivity of SnO₂ material for gas sensing, as well as reduce the sensing temperatures and the response time because the catalytic effect and electron donor of carbon crystallite [Qu, Wang, Chen, Han, & Lin, 2016]. First, the carbon matrix can accommodate the volume variations of SnO₂ core and avoid its pulverization. Second, the carbon shell can enhance the electrode conductivity, resulting a high reversible capacity. Third, the carbon with inert nature is less harmful under physiological/environmental conditions [Zhang, Wang, Zhang, Shao, Hu, & Shao, 2015]. Therefore, the SnO₂@carbon (SnO₂@C) hybrid nanoparticles (NPs) may retain the properties of individual components and further enhanced properties (such as optical, electrical, and catalytic property) and even present new synergistic effect.

Recently, the wrapping of a two-dimensional (2D) carbonaceous matrix outside core-shell NPs was shown to be a highly effective approach to enhance the conductivity and structural stability of core-shell NPs-based electrode materials [Gan, Lv, Sun, Shi, & Liu, 2016]. In this work, we synthesized SnO₂@C by hydrothermal carbonization of glucose in the presence of sodium stannate, and subsequent functionalization by 2D graphene oxide (GO). In such a sandwich like architecture, the volume expansion of the enwrapped SnO₂ NPs can be greatly controlled by the carbon shells. Moreover, the intimate contact between GO and SnO₂@C is favorable for accessibility to analytes and rapid diffusion of electrons. And further, a new

modified electrode was constructed by immobilization of the $\text{SnO}_2@\text{C}@\text{GO}$ nanocomposite on a glassy carbon electrode (GCE) surface. The resulting modified electrode was successfully applied to the determination of maltol in food samples with amplified electrochemical response and satisfactory recovery, which showed many merits such as easy fabrication, low cost, high sensitivity, and good reproducibility.

2. Experimental section

2.1. Chemicals and apparatus

Graphite flakes, nitric acid (HNO_3), sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), 3-aminopropyltrimethoxysilane (APTES), glucose and sodium stannate monohydrate ($\text{Na}_2\text{SnO}_3\cdot\text{H}_2\text{O}$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Maltol was obtained from Aladdin Industrial Inc. All reagents were of analytical grade. The buffer involved in this work was boric acid–borax buffer (pH 8.2). All chemicals in this work were used as received without further purification. Deionized water was used throughout the study.

The CHI 660D electrochemical workstation (Chenhua Instrument Limited Company, Shanghai, China), a traditional three-electrode system containing saturated calomel electrode (SCE) as the reference electrode, Pt wire as the counter electrode, and 3 mm GCE as the working electrode were used for electrochemical measurements. Powder X-ray diffraction patterns (XRD) of samples were recorded using a Rigaku D/Max-rC powder diffractometer in the 2θ range of $10\text{--}80^\circ$ with a 2θ step size of 0.01° and step time of 2 s. Raman spectra measurements were carried out on a micro-Raman spectrometer (Witech CRM200, the excitation wavelength at 532 nm). Scanning electron microscope (SEM) images were conducted on a Hitachi S-4800

instrument operating at 20 kV. Transmission electron microscope (TEM) images were obtained with a field-emission transmission electron microscope at an accelerating voltage of 200 kV (Tecnai G220 S-Twin, FEI Company, Netherlands).

2.2. Synthesis of SnO₂@C@GO nanocomposite

In a typical synthesis of SnO₂@C core-shell nanospheres [Hu, Yan, Shen, & Zhong, 2012], 4.0 g glucose and 0.214 g Na₂SnO₃·H₂O were dissolved in 40 mL water for 10 min. The aqueous solution was then transferred to a 50 mL Teflon-lined stainless steel autoclave, which was heated at 160 °C for 15 h. Afterward, the precipitates were separated by means of centrifugation at 4,000 rpm for 10 min. The product was washed six times with water and ethanol alternately, and dried in a vacuum oven at 70 °C for 12 h.

For the synthesis of highly conducting GO, a mild bulk synthesis approach was used [Kumar et al., 2015]. Firstly, tattered graphite was obtained by refluxing graphite flakes in concentrated HNO₃ for 24 h followed by washing with water and drying. This tattered graphite (1 g) was ground together with KMnO₄ until homogeneous. Concentrated H₂SO₄ (98%, 30 mL) was introduced into a 250 mL flask immersed in ice-bath, then the above mixture of tattered graphite and KMnO₄ was added pinch by pinch under vigorous stirring over 30 min. When the addition was completed, ice bath was removed and stirring was continued at room temperature till the volumetric expansion was once observed (about 30 min). The flask was placed in an ice-bath again and 120 mL water was added with rapid stirring. The temperature of the bath was raised to 90 °C and the stirring was kept for 1 h to obtain a homogeneous black suspension. Afterwards, the precipitates were separated by means of centrifugation at 12,000 rpm for 20 min and washed with water-methanol mixture (1:1, V/V) for

several times until pH was neutral. In order to fully exfoliate the GO sheets, the obtained precipitates were further suspended in water and ultrasonicated for 12 h.

GO was wrapped outside SnO₂@C core-shell nanospheres through electrostatic attraction. Firstly, 0.2 g SnO₂@C nanospheres were dispersed into 100 mL ethanol through ultrasonication. Then 1 mL APTES was added and refluxed for 5 h to get amine-functionalized SnO₂@C nanospheres. The products were separated by means of centrifugation at 4,000 rpm for 10 min and rinsed with ethanol to wash away the unreacted APTES. After that, 30 mL of GO aqueous solution (1 mg mL⁻¹) was added and the mixture was stirred vigorously for 1 h. Finally, the resulting SnO₂@C@GO was filtered, washed with water and ethanol several times, and redispersed into 5 mL water. The schematic illustration of the synthesis is presented in Fig. 1.

2.3. Electrode modification

Prior to modification, GCE was subsequently polished with 1.0 and 0.05 μm alumina powder on polishing cloth and sonicated successively in water-ethanol mixture (1:1, V/V) and water in order to remove adsorbed particles. The procedure for the fabrication of SnO₂@C@GO/GCE was conducted by casting 10 μL of SnO₂@C@GO suspension on the pretreated GCE surface and allowed to dry under an infrared lamp in the air.

2.4. Food samples preparation

The crispness biscuit, black beer, Cabernet Sauvignon red wine and orange juice samples were purchased from local market. Among them, the beer, red wine and juice samples were used directly, but biscuit sample was used after pretreatment. In an agate mortar, 10 g of biscuit sample was ground to powder, which was then stirred

with 150 mL absolute ethanol for 30 min. The filtrate of the solution was collected after being vacuum filtered and diluted in 50 mL volumetric flasks using water.

2.5. Determination of maltol

Maltol determination was performed by using boric acid–borax buffer with pH 8.2 as supporting electrolyte. After a 60 s accumulation time under open circuit and 5 s of quiet time, the square wave voltammograms were recorded from 0.10 to 0.90 V, and the oxidation peak current at 0.55 V was measured for maltol. The amplitude was 25 mV, the frequency was 15 Hz, and the scan rate was 40 mV s⁻¹.

3. Results and discussion

3.1. Characterizations

The structures of the as-prepared SnO₂@C@GO nanocomposite were identified with XRD, as shown in Fig. 2A. The diffraction peaks at 2θ values of 26.4° (110), 33.7° (101), 37.7° (200), 51.6° (211), 54.2° (220), 58.3° (002), 61.5° (310), 65.2° (112), 71.3° (202) and 78.3° (321) are consistent with the standard XRD data for the tetragonal rutile like SnO₂ phase (JCPDS File no. 41-1445). The mean crystal size calculated for SnO₂ nanoparticles that assemble into the SnO₂ core is found to be 7.6 nm by using the Scherrer equation. Besides, the peak at $2\theta = 10.4^\circ$ is in agreement with the (001) reflection of GO with an interlayer spacing of 0.81 nm. The results prove that SnO₂ nanoparticles coexist with GO sheets. Above all, no other impurity peaks are detected, indicating the high purity of the products.

Raman analysis, which provides information about atomic structure, is particularly useful for characterizing carbon-based materials. Fig. 2B shows the Raman spectra of

SnO₂@C (a) and SnO₂@C@GO (b) hybrid materials that contain a strong band at ~1590 cm⁻¹ (G band) and a weak band at ~1350 cm⁻¹ (D band). The G band in Raman spectra is well known to represent the E_{2g} vibrational mode of sp²-bonded graphitic carbon, and the D band is attributed to disordered structures resulting from atomic-scale defects on the graphitic plane [Maslova, Ammar, Guimbretiere, Rouzaud, & Simon, 2012]. A strong G band such as that can be seen in Fig. 2B often denotes an abundance of ordered carbon atoms in carbonaceous materials. The degree of crystallinity can also be quantified from the Raman spectrum by using the ratio of I_D/I_G , where I_D and I_G are the integrated intensities of the D and G band, respectively. The value of I_D/I_G calculated from curve a is relatively large at 0.67, implying a low degree of crystallinity as compared to that of crystalline graphite ($I_D/I_G = 0.1-0.3$) [Matthews, Pimenta, Dresselhaus, Dresselhaus, & Endo, 1999]. When GO is further wrapped outside of the SnO₂@C spheres, the D/G intensity ratio increases to 0.82 due to the oxygen functional groups in the GO sheets. However, the observed I_D/I_G of SnO₂@C@GO in our work is much lower than that of graphene based materials in other literatures [Zhou, Li, Sun, & Yang, 2016; Huang, Shuai, & Zhang, 2016], implying the low sp² C-network rupture, long range ordering and high enough electrical conductivity of graphene sheets, which originates from the mild oxidation process of graphite to prepare GO. The positive shifting in G band peak position compared with pristine graphene can be addressed to the hybridization of GO with an electron acceptor component (amino-functionalized SnO₂@C) [Zhu, Chen, & Liu, 2012], which can modify the electronic structure of GO by stiffening or softening of phonons and give rise to the shift of Fermi energy level [Das, Voggu, Routa, & Rao, 2008; Voggu, Rout, Franklin, Fisher, & Rao, 2008]. Next to the G band shows the D' band which is due to the presence of disorder (Fig. 2B, curve b). This band is

dispersive in the frequency because of the double resonant scattering [Thomsen, & Reich, 2000; Maslova et al., 2012], however, the relative intensity of this band is usually low. In addition, the SnO₂@C@GO samples produce a distinct 2D band at around 2700 cm⁻¹ in their Raman spectra (Fig. 2B, curve b), which arises from the second order of zone-boundary phonons [Jiang et al., 2011], and S3 peak near 2950 cm⁻¹ shows up which can be attributed to the lattice disorders with its number of Raman shift roughly the combination of the G and D peaks. The 2D band shifts to a higher frequency (2700 cm⁻¹) from the typical peak (2679 cm⁻¹) of a single layer structure, indicating the possible multilayer structure of GO samples wrapped outside of SnO₂@C spheres.

Morphology of the as-prepared samples were investigated by SEM and TEM images, as shown in Fig. 3. The SEM image in Fig. 3a shows that the size of SnO₂@C nanospheres prepared by our one-pot method is quite uniform. From the magnification image (Fig. 3b), sphere-like morphology with the average size of 68 nm is observed, which can be assigned to the 3D structure of the SnO₂@C. To better understand the core-shell structure, the obtained sample can be further confirmed by TEM (Fig. 3c,d). TEM image shows that SnO₂ cores (dark spots in Fig. 3c) with uniform sizes (~58 nm) are assembled by numerous SnO₂ nanoparticles (~7.6 nm), and these SnO₂ cores are further effectively encapsulated within the well-proportioned spherical carbon (~10 nm). To study the detailed lattice structure, the high-resolution TEM image was carried out. The interplanar distance is 0.337 nm, corresponding to the (110) plane of rutile SnO₂ (Fig. 3d). Furthermore, Fig. 3e and f show the TEM images of SnO₂@C@GO ternary architecture. Clearly, the 2D, free-standing GO with thin stacked flakes and layered structure at the edge can be seen in Fig. 3e, which is flat but crumpled. In addition, the core-shell structure of

SnO₂@C is well maintained. And the high-magnification TEM image of SnO₂@C@GO is shown in Fig. 3f. It is apparent that SnO₂@C nanospheres are well wrapped by the transparent GO textures because of interfacial interactions. The wrapping of SnO₂@C nanospheres with GO can be explained by the electrostatic interaction of the -OH and -COOH functional groups of GO with the surface of amino-functionalized SnO₂@C. Notably, the intimate contact between conductive GO sheets and SnO₂@C nanospheres can not only enhance the conductivity of overall electrode but also is favourable to the transfer of electrons to active SnO₂@C materials.

Electrochemical impedance spectroscopy (EIS) is a tool to evaluate the electron transfer resistance, which was carried out to investigate the conductivity of the modified electrode. Supplemental Fig. S1 shows the Nyquist plots recorded for bare GCE, SnO₂@C/GCE and SnO₂@C@GO/GCE in a 5 mM K₃Fe(CN)₆ solution with 0.1 M KCl as the supporting electrolyte. The Randles equivalent circuit simulating with ZSimWin software in the inset of Supplemental Fig. S1 includes the resistance of solution (R_s), the double layer capacitance (C_{dl}), the electrode transfer resistance (R_{et}) and the Warburg impedance (Z_w). The modification of the electrode surface only affects the value of R_{et} , which denotes the semicircle diameter of the Nyquist plots and is an appropriate signal exhibiting the interfacial natures of the modified electrodes. The EIS result of GCE modified by SnO₂@C shows that the R_{et} greatly decreases from 1566.3 (curve a) to 763.1 Ω (curve b). This effect is attributed to SnO₂@C core-shell structured nanospheres, which serve as a good-conducting layer and increase the interfacial electron transfer between the electrode and the K₃Fe(CN)₆ probe. When the SnO₂@C@GO is coated on the surface of GCE (curve c), an interfacial electron transfer is further accelerated, which leads to a significant decrease

of R_{et} value ($\sim 381.5 \Omega$). Such improved performance is the result of a synergistic effect arising from the interactions between SnO_2 and carbon as well as between $\text{SnO}_2@\text{C}$ and GO. In such hybrid systems, the $\text{SnO}_2@\text{C}$ not only provides a high catalytic ability, but also serves as a nanospacer to maintain the adjacent GO sheets separated to minimize the agglomeration of GO sheets.

3.2. Electrochemical behavior of maltol

The electrochemical behavior of maltol was investigated at different modified electrodes using cyclic voltammetry (CV) in pH 8.2 boric acid–borax buffer. Supplemental Fig. S2 shows cyclic voltammograms recorded at bare GCE and $\text{SnO}_2@\text{C}@GO/\text{GCE}$ in the absence and in the presence of $10 \mu\text{M}$ maltol at a scan rate of 100 mV s^{-1} . As shown in curve a, a tiny peak with the oxidation peak potential at about 0.58 V is clearly observed on bare GCE, suggesting that the oxidation activity of maltol is very low on the bare GCE surface. Interestingly, the oxidation peak increases significantly on the surface of $\text{SnO}_2@\text{C}@GO$ –modified GCE (curve b), indicating that the prepared $\text{SnO}_2@\text{C}@GO$ is more active for the oxidation of maltol. Compared with bare GCE, $\text{SnO}_2@\text{C}@GO$ ternary core–shell material is proven to own larger electrode area and faster electron transfer rate, therefore, the oxidation activity of maltol is improved obviously on $\text{SnO}_2@\text{C}@GO$ surface. In addition, it is obvious that the oxidation peak current of maltol decreases markedly during the second and third anodic sweeps. This phenomenon manifests the strong adsorption of oxidation product of maltol on electrode surface. Consequently, the oxidation peak current in the first anodic sweep is recorded for the analysis of maltol to achieve high sensitivity. Additionally, the CV responses of bare GCE (curve c) and $\text{SnO}_2@\text{C}@GO/\text{GCE}$ (curve d) in the absence of maltol were also studied, showing

virtually featureless curves. This reveals that the oxidation peaks in Supplemental Fig. S2 are attributed to maltol.

The electrochemical responses of maltol were further examined using square wave voltammetry (SWV), and the results are displayed in Fig. 4A. In pH 8.2 boric acid–borax buffer and after 60-s accumulation, one negligible oxidation peak is observed on the bare GCE (curve a), indicative of slow electron transfer, whereas the response is considerably improved by 2.2 times at $\text{SnO}_2\text{@C}/\text{GCE}$ (curve b). The enhancement in the peak current at the surface of $\text{SnO}_2\text{@C}$ is due to the coating of carbon shell, the $\text{SnO}_2\text{@C}$ core–shell structure can combine the merits of good contact and efficient diffusion distances for electron transport, which leads to fast reaction kinetics. However, it is necessary to be noted that the oxidation signal of maltol on the surface of $\text{SnO}_2\text{@C@GO}$ is 5.0 times bigger than that on bare GCE (curve c). The result reveals that the incorporation of 2D GO sheets can significantly improve the electrochemical performance of $\text{SnO}_2\text{@C}$ electrode. It may be resulted from the synergistic effect that the $\text{SnO}_2\text{@C}$ nanospheres act as cores support to improve the 2D GO sheets stability and the 2D GO sheets serve as flexible coating and conductive network for $\text{SnO}_2\text{@C}$ nanospheres. Furthermore, the 2D GO sheets protect against the volume changes of $\text{SnO}_2\text{@C}$ nanospheres during electrochemical processes. Additionally, the SWV response of $\text{SnO}_2\text{@C@GO}/\text{GCE}$ in the absence of maltol is also studied (curve d), no oxidation wave is clearly observed. In conclusion, the comparisons of Supplemental Fig. S2 and Fig. 4A clearly suggest the potential of $\text{SnO}_2\text{@C@GO}$ –based sensing platform for highly sensitive electrochemical detection.

3.3. Electrochemical oxidation mechanism of maltol

The electrochemical behaviors of maltol on $\text{SnO}_2\text{@C@GO}/\text{GCE}$ with different

scan rates were examined using CV. As seen in Fig. 4B, an oxidation peak is observed for maltol, and the oxidation peak current (I_p , μA) increases linearly with the scan rate (ν , mV s^{-1}) (Inset I of Fig. 4B). So the oxidation of maltol is an adsorption-controlled irreversible process. For the irreversible and adsorption-controlled oxidation reaction, the relationship between peak potential (E_p , V) and scan rate can be expressed by the following Laviron's equation [Laviron, 1974]:

$$E_p = E^0 + \left(\frac{RT}{\alpha nF}\right) \ln\left(\frac{RTk^0}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right) \ln \nu \quad (1)$$

where E^0 is the formal potential, α is the electron-transfer coefficient, n is the number of transferred electron, k^0 is the rate constant of heterogeneous electron transfer, and other symbols have their usual meanings. It can be found in the inset II of Fig. 4B that the E_p is proportional to $\ln \nu$, and the slope $RT/\alpha nF$ equals to 0.047. So the value of αn is calculated to be 0.55. Generally, α is considered to be 0.5 in an irreversible electrode reaction. Consequently, one electron is involved in the oxidation of maltol, consisting with the reported results [Chao et al., 2014; Ma et al., 2014].

The oxidation peak potentials of maltol in boric acid-borax buffer solutions with different pH values were studied to discuss the number of transferred protons. The results show that E_p moves negatively with increasing the pH value, and the slope value is -60 mV pH^{-1} . This is close to the theoretical -59 mV pH^{-1} , indicating the equal number of transferred protons and electrons. Based on the above results, it can be concluded that the electrochemical oxidation of maltol is a one-electron and one-proton process:

3.4. Optimization of parameters for maltol detection

The oxidation behaviors of 5.0 μM maltol in various media such as pH 2.6–5.4 acetic acid–sodium acetate buffer, pH 5.8–8.0 phosphate buffer, pH 7.4–9.0 boric acid–borax buffer, pH 1.81–6.59 Britton–Robinson buffer, and HCl, H_2SO_4 , HClO_4 , NaOH solution, were studied by SWV. The excellent oxidation response is obtained in boric acid–borax buffer for maltol since the peak shape is well-defined. In boric acid–borax buffer, the oxidation peak currents of maltol on $\text{SnO}_2@\text{C}@\text{GO}/\text{GCE}$ increase gradually with pH value from 7.4 to 8.2, and then gradually decrease with further increasing pH value to 9.0 (Supplemental Fig. S3). To achieve the high sensitivity, pH 8.2 boric acid–borax buffer was used for the determination of maltol.

The effect of amount of $\text{SnO}_2@\text{C}@\text{GO}$ suspension on the oxidation signals of 5.0 μM maltol was also investigated, as shown in Supplemental Fig. S4. The oxidation peak currents of maltol enhance significantly when improving the amount of $\text{SnO}_2@\text{C}@\text{GO}$ suspension from 0 to 10 μL , due to the improved accumulation efficiency of maltol caused by $\text{SnO}_2@\text{C}@\text{GO}$ adsorption. As further increasing the amount of $\text{SnO}_2@\text{C}@\text{GO}$ suspension to 15 μL , the oxidation peak currents of maltol change slightly, indicative of a saturation status for maltol adsorption. So 10- μL $\text{SnO}_2@\text{C}@\text{GO}$ suspension was selected to modify the GCE surface.

In order to further improve the detection sensitivity, accumulation is a simple and effective approach, which mainly contains potential and time parameters. The oxidation peak currents of 5.0 μM maltol were compared after 60 s accumulation under different potentials by SWV (Supplemental Fig. S5A). The peak currents almost keep constant as accumulation potential positively shifting from -0.2 to 0.4 V, revealing that the accumulation potential causes no influence on the oxidation peak

current of maltol at the SnO₂@C@GO-modified GCE. Consequently, an open-circuit accumulation was performed.

The effect of accumulation time on the peak current of 5.0 μM maltol was further explored (Supplemental Fig. S5B). The peak currents increase rapidly within the first 60 s and then level off, signifying that the accumulation of maltol is very rapid to reach saturation at the SnO₂@C@GO film.

3.5. Chronocoulometry measurements

In next study, chronocoulometry technique was used to determine the kinetics in the electro-oxidation of maltol at bare GCE and SnO₂@C@GO/GCE. According to the formula given by Anson [Anson, 1964]:

$$Q = \frac{2nFAcD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads} \quad (3)$$

where F is the Faraday constant, A is the geometrical area of the GCE (0.071 cm²), c is the concentration of maltol (10 μM), D is the diffusion coefficient, t is the time, Q_{dl} is the double-layer charge which can be eliminated by the subtraction of the background charge, Q_{ads} is the Faradaic charge due to the oxidation of adsorbed maltol molecules. Other symbols have their usual meanings. The slope of the $Q-t^{1/2}$ plots can be expressed as $2nFAcD^{1/2}/\pi^{1/2}$. Here, $n = 1$, $\pi = 3.14$, and the slope values are 0.328 and 1.361 μC s^{-1/2} for bare GCE and SnO₂@C@GO/GCE, respectively. The calculated values of 1.80×10⁻⁵ and 3.09×10⁻⁴ for D and the values of 0.0506 and 0.399 μC for Q_{ads} at bare GCE and SnO₂@C@GO/GCE can be obtained, respectively. According to the following equation

$$Q_{ads} = nFA\Gamma \quad (4)$$

the surface coverage (Γ) is 7.39×10⁻¹² and 5.82×10⁻¹¹ mol cm⁻² for bare GCE and

SnO₂@C@GO/GCE, respectively. The results give prominent evidence that the SnO₂@C@GO composite on electrode surface shows enlarged accumulation ability for maltol.

3.6. Analytical performances

The potential interferences for the detection of maltol were also studied. It is found that 2 mM K⁺, NO₃⁻, Na⁺, Cl⁻, Ca²⁺, NH₄⁺, HCO₃⁻, glucose, sucrose, starch, glycine, citric acid, tartaric acid; 1.5 mM SO₄²⁻, Mg²⁺, H₂O₂; 0.5 mM Al³⁺, Zn²⁺; 0.1 mM ascorbic acid and 10 μM hydroquinone do not interfere with the oxidation signal of 1.0 μM maltol (the peak current change is below 5%).

The reproducibility between multiple SnO₂@C@GO/GCEs was evaluated by parallel determining the oxidation peak currents of 1.0 μM maltol. The relative standard deviation (RSD) is below 4% for ten SnO₂@C@GO/GCEs, suggesting excellent reproducibility and detection precision.

In order to evaluate the capability of the developed modified electrode in the detection of maltol, the response behaviors of maltol with different concentrations were examined. As shown in Fig. 5, the oxidation peak current of maltol on SnO₂@C@GO/GCE (*I_p*, μA) is linear with its concentration (*c*, μM) over the range from 0.08 to 10 μM. The linear regression equation is $I_p = -0.0159 + 0.154c$, and the correlation coefficient (*R*) is 0.998, revealing good linearity. After an accumulation of 60 s, the detection limit is calculated to be 12 nM based on three signal-to-noise ratio.

The analytical characteristics of the developed electrode are compared with those of previously reported maltol voltammetric methods. The comparison results are summarized in Supplemental Table 1. According to the data of the table, the

represented analytical characteristics of our developed electrode are better or at least comparable with those of the other depicted electrodes. We highlight that the features of the proposed system are its precision, sampling throughput, low consumption of reagent and of sample solution, no need for a pretreatment step, and excellent repeatability.

3.7. Practical application

To evaluate the practical application of this new method, it was used to detect the content of maltol in different food samples including biscuit, beer, red wine and juice (Supplemental Fig. S6). Upon addition of 100 μ L sample solution into 5.0 mL pH 8.2 boric acid–borax buffer, the SWV curves were recorded from 0.1 to 0.9 V after 60–s accumulation (curve a). The determination of each sample was performed six replicates, and the RSD was lower than 4%, revealing good precision. The content of maltol was obtained by the standard addition method (curve b), and the results are listed in Table 1. Moreover, the values of recovery are also calculated to be over the range from 96.3 to 104%, indicating that the newly–developed method is accurate and has promising application.

4. Conclusion

In summary, we have presented an effective method to prepare SnO₂@C core–shell nanospheres supported on graphene oxide (SnO₂@C@GO). SnO₂ particles were encapsulated by carbon shell under one–step hydrothermal condition and then the wrapping of SnO₂@C by GO sheets was performed. The SnO₂@C@GO nanocomposite was employed as a new electrochemical enhanced material for the fabrication of electrochemical platform for determination of maltol in food, which

showed good linear range (0.08~10 μM) and low detection limit (12 nM). We believe the proposed detection approach opens up a new electrochemical detection strategy, extends the application range of semiconductor materials, and sheds light on the further fusing of electrochemical technique and analytical methods.

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Figure captions

Fig. 1 Schematic representation of the fabrication of SnO₂@C@GO modified GCE.

Fig. 2 (A) Powder XRD of SnO₂@C@GO. (B) Raman spectra of SnO₂@C (a) and SnO₂@C@GO (b).

Fig. 3 SEM (a,b) and TEM (c–f) images of SnO₂@C (c,d) and SnO₂@C@GO (e,f).

Fig. 4 (A) SWV graphs of bare GCE (a), SnO₂@C/GCE (b) and SnO₂@C@GO/GCE (c) in pH 8.2 boric acid–borax buffer containing 4.0 μ M maltol. Curve d corresponds to the SW voltammogram of SnO₂@C@GO/GCE in a blank solution. Accumulation time = 60 s, amplitude = 25 mV, frequency = 15 Hz. (B) Cyclic voltammograms of 10 μ M maltol in pH 8.2 boric acid–borax buffer at SnO₂@C@GO/GCE with different scan rates, including 100 (e), 125 (f), 150 (g), 175 (h), 200 (i), 225 (j) and 250 (k) mV s⁻¹. Insets: linear relationship of I_p vs. ν (I) and E_p vs. $\ln \nu$ (II).

Fig. 5 SWVs of SnO₂@C@GO/GCE in different concentrations of maltol: 0.08, 0.5, 1.0, 3.0, 5.0, 6.5, 8.0, 10 μ M (from a to h). The inset shows the calibration plot of maltol vs. peak current.

Table 1 Detection and recovery of maltol in biscuit, beer, red wine and juice samples.

Sample	Detection		Recovery test		
	This method (M)	RSD (%)	Spiked (M)	Found (M) ^a	Recovery (%) ^b
Biscuit	1.85×10^{-7}	3.9	1.00×10^{-7}	1.01×10^{-7}	101
Beer	3.71×10^{-7}	3.0	3.00×10^{-7}	2.89×10^{-7}	96.3
Red wine	1.57×10^{-7}	2.7	3.00×10^{-7}	2.92×10^{-7}	97.3
Juice	—	—	5.00×10^{-7}	5.20×10^{-7}	104

^a Found (M): the found value (c'_s) is calculated according to the equation:

$$\frac{I_{p2}}{I_{p1}} = \frac{c_0 + c'_s}{c_0}, \text{ where } I_{p1} \text{ and } I_{p2} \text{ correspond to the peak current of maltol before and}$$

after spiking. c_0 is the concentration of maltol that exists in original sample (i.e., column 2).

^b Recovery (%): the recovery value is calculated through dividing c'_s by the real spiked value (c_s , column 4)

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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