Analytical Methods

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

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A B S T R A C T

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 ($SnO_2@C@GO$). The morphological and components properties of $SnO_2@C@GO$ 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. $SnO_2@C@GO$ 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 for complex food matrices.

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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 poten-

tial 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 &

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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, 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, Hu, et al., 2015; Gan, Shi, Wang, et al., 2016; 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 SnO_2-based anode with improved specific capacity and cycling stability, making it more promising for use in lithium ion batteries (Liu et al., 2016). Qu et al. found the carbon crystallite on SnO_2 grain boundary could improve the sensitivity and selectivity of SnO_2 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 SnO_2 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 et al., 2015). Therefore, the SnO_2@carbon (SnO_2@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 SnO_2@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 SnO_2 NPs can be greatly controlled by the carbon shells. Moreover, the intimate contact between GO and SnO_2@C is favorable for accessibility to analytes and rapid diffusion of electrons. And further, a new modified electrode was constructed by immobilization of the SnO_2@C@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 ($Na_2SnO_3 \cdot H_2O$) 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 10–80° 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 SnO_2@C@GO nanocomposite

In a typical synthesis of SnO_2@C core-shell nanospheres (Hu, Yan, Shen, & Zhong, 2012), 4.0 g glucose and 0.214 g $Na_2SnO_3 \cdot H_2O$ 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 4000 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 HNO_3 for 24 h followed by washing with water and drying. This tattered graphite (1 g) was ground together with $KMnO_4$ until homogeneous. Concentrated H_2SO_4 (98%, 30 mL) was introduced into a 250 mL flask immersed in ice-bath, then the above mixture of tattered graphite and $KMnO_4$ 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 SnO_2@C core-shell nanospheres through electrostatic attraction. Firstly, 0.2 g SnO_2@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 SnO_2@C nanospheres. The products were separated by means of centrifugation at 4000 rpm for 10 min and rinsed with