Hierarchical triple-shelled porous hollow zinc oxide spheres wrapped in graphene oxide as efficient sensor material for simultaneous electrochemical determination of synthetic antioxidants in vegetable oil

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Abstract

Hierarchical triple-shelled porous hollow zinc oxide spheres (ZnO TPHS) were conveniently synthesized via a hard template method. And the ZnO TPHS were then wrapped into graphene oxide (GO) nanosheets through electrostatic attraction after being amino-functionalized. The composition of ZnO TPHS@GO hybrid was determined using energy dispersive X-ray spectroscopic analysis, X-ray diffraction and Raman spectra. The morphology of ZnO TPHS@GO hybrid was comprised of ZnO nanoparticles and ultrathin GO nanosheets that were characterized with scanning electron microscopy and transmission electron microscopy. The porous hollow structure and intimate contact between ZnO TPHS and GO interfaces provided a large surface area and high electron transfer activity for synthetic antioxidants in an acidic electrolyte. Based on this, a novel electrochemical sensor for the simultaneous determination of tert-butylhydroquinone (TBHQ) and butylated hydroxyanisole (BHA) has been constructed using ZnO TPHS@GO as sensing material. Under optimal conditions, the developed sensor exhibited excellent electrochemical responses in the co-detection of TBHQ and BHA, with limits of detection of 0.137 and 0.0488 μM ($S/N = 3$), respectively. Besides, the selectivity, reproducibility and application in edible vegetable oil samples were also investigated. This study proposed a novel method of fabrication of metal oxide-decorated GO-based materials for the fabrication of sensitive electrochemical sensors that met the needs of food safety control.

Keywords: ZnO, Graphene oxide, tert-Butylhydroquinone, Butylated hydroxyanisole, Electrochemical sensor

1. Introduction

Synthetic antioxidants are a group of chemicals typically found in cosmetic formulations, rubber, elastomers, plastic, waters, pharmaceuticals and foods at low concentrations to markedly delay or prevent the oxidation process [1,2]. One of the most commonly employed synthetic antioxidants is tert-butylhydroquinone (TBHQ), which can not only prevent rancidification of food and extend the shelf-life but also have advantages of wide availability, low cost, high thermal stability and anti-lipid peroxidation activity [3]. Moreover, butylated hydroxyanisole (BHA) strengthens the antioxidative efficiency of TBHQ which is also a synthetic antioxidant [4]. So these two compounds are often added to foodstuffs in combination because of their synergistic antioxygenation. However, studies demonstrated that an excess use of antioxidants may lead to a loss of sustenance, affect food quality and endanger human health [5]. Furthermore, some antioxidants metabolites were reported to generate peroxides in mice and rats and may induce cellular DNA damage or have the capacity to be cancer initiators [6]. Therefore, their contents in processed food have been strictly restricted in most countries. For example, the addition of TBHQ and BHA in soft drinks is not authorised by the European Union (Directive 95/2/EC), and the maximum permitted level in flavourings is 200 mg kg⁻¹ [7]. Based on this, an effective and convenient quantification method for monitoring the levels of antioxidants is necessary to fulfillment of the legal requirements as well as quality control procedures in the food industries.

In fact, analysis becomes difficult at trace concentrations without prior separation because the antioxidants are chemically similar. The present state of the art in simultaneous antioxidant analysis involves high-performance liquid chromatography (HPLC) [8,9], chemometric approach [10], gas chromatography-tandem mass

spectrometry [11], batch injection analysis [12], spectrofluorimetric method [13,14], capillary electrophoresis [15], and so on. But all of these methods, especially those involving chromatography, are generally time-consuming due to the pre-extraction steps, need highly toxic solvents and in some situations require rather expensive complicated equipment. An efficient alternative method to those discussed above is the voltammetric technique [16–22], owing to its fast response, high sensitivity, simplicity, on site analysis without sample cleanup, low cost and portable instrumentation.

Very recently, hollow micro-/nanostructured capsules with multiple shells have stimulated researchers' great interest because of their beneficial characteristics, such as low density, large internal void space, high surface area, material saving, and potential applications in various fields [23]. Compared with simple hollow sphere, the hollow multi-shelled hetero-structures can maximize the advantages of hollow nanostructures due to their higher active surface area per unit volume and larger volume occupying rate [24]. For example, the multi-shelled Co_3O_4 hollow microspheres exhibited higher capacitance of 394.4 F g^{-1} at the current density of 2 A g^{-1} than many nanostructured Co_3O_4 [25], indicating facilitated electrolyte penetration and more active sites for electrochemical reactions. Hu et al and coworkers confirmed that the electrochemical performance of $\alpha\text{-Fe}_2\text{O}_3$ porous multi-shelled hollow spheres was superior to those of the state-of-the-art Fe_2O_3 when using as an anode material for lithium ion batteries, attributing to the hierarchical porosity, special micro/nanostructure, shorter electron and lithium ion diffusion pathways [26]. Furthermore, the triple-shelled CeO_2 catalysts showed much higher catalytic activities than double-shelled, single-shelled and commercial CeO_2 [27], which was thought to be related to the catalysts' confined interior space that might improve the reaction conversion. Among all metal oxides, zinc oxide (ZnO) has been regarded as the promising electrode material because of its

outstanding electronic characteristic, high catalytic activity, environmental friendliness, low cost, etc [28]. As a result, the design of ZnO hollow spheres with multiple shells of electrochemical catalyst is both important and interesting.

In this paper, triple-shelled porous hollow ZnO spheres (ZnO TPHS) were successfully synthesized with the assistance of carbon microspheres as hard templates. Zinc precursor-carbon microspheres composites were facile prepared by the hydrolysis of glucose and simultaneously the adsorption of Zn^{2+} . The ZnO TPHS with isolated chambers could be created after disintegrating the carbon microspheres by calcination in air. Thereafter, graphene oxide (GO) nanosheets with sufficient active oxygen sites and highly negative surface charge were coated on amino-functionalized ZnO TPHS to improve the electrochemical performance, enhance the dispersion and prevent a structural collapse of ZnO TPHS catalyst. When evaluated as electrode material for electrochemical sensors, the ZnO TPHS@GO exhibited confined interior spaces, numerous surface active sites and high permeability, which promoted the efficiency for the simultaneous sensing of TBHQ and BHA in terms of sensitivity, stability and selectivity.

2. Experimental

2.1. Materials and instruments

TBHQ and BHA were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Heptahydrate zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), dextrose monohydrate (glucose, $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$), 3-aminopropyltrimethoxysilane (APTES), graphite flakes, sodium nitrate (NaNO_3), nitric acid (HNO_3), sulphuric acid (H_2SO_4), potassium permanganate (KMnO_4) and hydrogen peroxide (H_2O_2) were purchased from Sinopharm Chemical

Reagent Co., Ltd. All chemicals were analytical grade and used without further purification except specific instruction. 0.01 M stock solution of TBHQ and BHA were prepared by dissolving TBHQ and BHA in absolute ethanol, respectively. Working solutions of TBHQ and BHA were prepared by appropriate dilution from their stock solutions. Ultrapure water (18.25 M Ω cm) was used throughout the experiment. Unless otherwise stated, all experiments were carried out at room temperature.

All electrochemical measurements were conducted on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). A conventional three-electrode system was employed with modified glassy carbon electrode (GCE) used as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The scanning electron microscopy (SEM) images were obtained with Hitachi S-4800 microscope (Japan). The transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopic analysis (EDX) were collected by Tecnai G220S-Twin microscope (FEI, Netherlands). Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer (Germany) equipped with a Cu-K α source ($\lambda = 1.5406 \text{ \AA}$). The scan rate was 2° min^{-1} and steps were 0.02° . Raman spectrum was performed using Withch CRM200 Raman spectrometer at a laser excitation wavelength of 532 nm.

HPLC was performed on an Agilent Series 1260LC instrument (Agilent Technologies, USA) equipped with an on-line degasser, a quaternary pump, a diode array detector (DAD), a column oven and an auto-sampler [9]. The antioxidants separation was conducted on a Hypersil-ODS C18 column (5 μm average particle size, 200 mm $\times$ 4.6 mm i.d.). The column temperature was achieved at 60 $^\circ\text{C}$. The mobile phase consisted of solvent A (methanol and acetonitrile (1:3, V/V)) and solvent B (5% acetic acid in water). The column was equilibrated in 20% A and the gradient elution

was as follows: 20–100% A over 2.5 min, hold at 100% A for 2.5 min, 100–20% A over 0.5 min, hold at 20% A for 2.5 min. Sample injection volume was 20 μL and the flow rate was continually maintained at 2 $\mu\text{L min}^{-1}$.

2.2. Preparation of ZnO TPHS@GO based sensor

ZnO TPHS was synthesized according to the literature [29]. Briefly, 4.0 g glucose was initially dissolved in 20 mL water, and then 10 mL $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ water solution (0.21 M) was poured into the glucose solution with vigorous stirring for 10 min at 298 K to get a clear and transparent solution. Afterwards, the mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave, which was then sealed, maintained at 180 °C for 20 h, and was cooled to room temperature naturally. The black precipitate was filtered off, washed with water and ethanol several times, and then dried at 80°C overnight.

For the synthesis of highly conducting GO, a mild bulk synthesis approach was used [30]. 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. 30 mL 98% concentrated H_2SO_4 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. Once the addition was completed, ice bath was removed and stirring was continued at room temperature till the volumetric expansion was 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 centrifugally, washed with water-methanol mixture for

several times until pH was neutral, and dried at 60 °C for 8 h.

Subsequently, 100-mL ethanol containing 0.2 g of ZnO TPHS was sonicated for 20 min for dispersion. Then 1 mL APTES was dropped into the above prepared solution slowly and followed with refluxing for 5 h. The product (ZnO TPHS-NH₂) was filtered and washed with ethanol. And then, 30 mg of the obtained GO powder was further suspended in 30 mL water and sonicated for 12 h to fully exfoliate the GO sheets. This GO aqueous solution was mixed with ZnO TPHS-NH₂ and stirred vigorously for 1 h. Finally, the resulting ZnO TPHS@GO was centrifuged, washed with ethanol and water for five times, and redispersed in 50 mL water.

In order to fabricate the sensor for TBHQ and BHA, the bare GCE (3 mm in diameter) was initially polished with alumina oxide slurries (0.3 and 0.05 μm in order) on a wet polishing cloth, followed by successive ultrasonic treatment in ethanol/water (1:1, V/V) and water for 3 min. Then, 10 μL of the ZnO TPHS@GO water suspension was cast on the pretreated GCE surface and allowed to dry under an infrared lamp in the air. The preparation procedure of ZnO TPHS@GO composite and the fabrication method of the sensor are shown in Scheme 1.

2.3. Measurement procedure

Unless otherwise stated, citric acid-Na₂HPO₄ buffer with pH 3.0 was used as supporting electrolyte for the simultaneous detection of TBHQ and BHA. Before the cyclic voltammetry (CV) measurements, the modified electrode was successively scanned between -0.3 and 1.0 V until stable cyclic voltammograms were obtained. For the square wave voltammetry (SWV) measurements between 0 and 0.80 V, a 60-s accumulation under open-circuit was used and the oxidation peak currents at 0.37 and 0.52 V were measured for TBHQ and BHA, respectively. Here, amplitude = 25 mV,

frequency = 10 Hz, scan rate = 40 mV s⁻¹. The response time for one determination was 80 s.

2.4. Vegetable oil samples pretreatment

The vegetable oil samples including peanut oil, soybean oil, sesame oil and colza oil were obtained from the local market and extracted for TBHQ and BHA analysis [31]. In a 10-mL centrifuge tube, 5 g of vegetable oil sample was mixed with 5.0 mL of pure methanol, and the mixture was agitated for 5 min. After being centrifuged at 3000 rpm for 5 min, the extracts were transferred into another 10-mL centrifuge tube. The above extraction procedures were repeated twice, and all the extracts were collected in a 25-mL conical flask, which was then diluted to the mark with methanol.

3. Results and discussion

3.1. Characterizations

The morphologies of the ZnO TPHS and ZnO TPHS@GO are shown in Fig. 1. The SEM image of the ZnO TPHS, as shown in Fig. 1A, shows the quasi-spherical shape and non-aggregation characteristics. Notably, the holes are observed in many spheres, indicating the hollow nature of the ZnO TPHS. The surfaces of ZnO TPHS are densely assembled by ZnO nanoparticles with an average diameter of ~70 nm, which are revealed by enlarged image of regional section (Fig. 1B). The TEM results are consistent with SEM images and provide additional evidence for the triple-shelled architecture. Fig. 1C indicates that the prepared triple-shelled porous hollow ZnO spheres show clear interiors and intermediate layers. The internal shells are not located in the central places of the sphere, as the large hollow regions make them free. The

outer, intermediate and inner shells of the triple-shelled structures have a diameter of 1.3, 0.48, and 0.16 μm , respectively, with a uniform thickness of 63, 50, and 37 nm. Simultaneously, the products possess monodisperse size distribution, uniform spherical morphology and rough surface. Moreover, high-resolution TEM image in Fig. 1D shows the clear lattice fringes with spacing of 0.25 nm, which corresponds to the (101) plane of wurtzite ZnO. The porous nature of the ZnO TPHS shells are readily accessible for analytes, and the internal void and hierarchical structure also ensure the structural stability, which contribute to enhanced electrochemical performances. The produced ZnO TPHS was then wrapped in GO, and the SEM image clearly shows that the high quality ultrathin GO layers are homogeneously and densely attached on the surface of ZnO TPHS (Fig. 1E). And the intimate contact between the GO nanosheets and ZnO TPHS can be observed. It is believed that the immobilization of ZnO TPHS on the surface of GO nanosheets prevents the stacking of GO nanosheets due to van der Waals interactions to a certain degree, leading to rich porous structure and a large available surface area for electrochemical reactions. On the other hand, the GO may play act as the soft support to improve the dispersion of ZnO TPHS and the electrical conductivity of the ZnO TPHS@GO composites. The detailed hetero-structure is further confirmed by TEM observation (Fig. 1F), which directly reveals that the shape and triple-shelled structure of the ZnO TPHS retain after GO wrapping.

In order to investigate the elemental composition and distribution in the ZnO TPHS@GO, EDX test was carried out and shown in Fig. 2A. It reveals that the C, O, and Zn elements are uniformly distributed in the three-layer shells, suggesting uniform deposition of ZnO nanoparticles in these shells. The Cu signal in the spectrum is from the TEM carbon film with copper grids. Moreover, the absence of any other detectable elements in the EDX data suggests the successful synthesis of ZnO TPHS@GO.

The phase purity and size of the prepared ZnO TPHS were determined by XRD analysis. The sharp and most intense peaks in Fig. 2B imply high crystalline nature and single phase of synthesized ZnO TPHS. The crystal planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) in the XRD patterns can be perfectly indexed to the hexagonal wurtzite structure of ZnO according to the JCPDS data of ZnO (card No. 36–1451), and the diffraction peak at a 2θ value of 10.4° can be attributed to the stacked GO sheet, which is consistent with the (001) interlayer spacing of 0.81 nm. In addition, no diffraction peaks from any other impurities are detected. For more evaluation, the size of ZnO TPHS is calculated using Debye–Scherrer equation [32]:

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is Scherrer constant depending on the shape of the particles (i.e., 0.89), λ is the wavelength of X-ray, θ and β are the Bragg diffraction angle and full-width at half-maximum data of the intense peak corresponding to plane (101) appears at 36.2° . The average particle size of the ZnO nanoparticles on the prepared ZnO TPHS shells is 71 nm.

Furthermore, the information of defects in ZnO TPHS@GO composite was described by Raman spectrum (Fig. 2C), which shows the low mode E_2 and high mode E_2 around 98 and 434 cm^{-1} , which correspond to the vibration of heavier components (cationic zinc) and lighter components (anionic oxide), respectively. The peak at 330 cm^{-1} is due to the multiple phonon scattering process of ZnO. And low defect density in the composite is verified by the weak peak of the secondary mode of 2 A1 (LO) at 576 cm^{-1} , arising from crystal defects like Zn interstitials (Zn_i) or oxygen vacancies (V_O) [33]. Besides, two additional prominent peaks located at around 1359 and 1594

cm^{-1} are observed for GO, which are the characteristic signals of disorder band associated with structural defects generated in graphene (D band) and the well ordered E_{2g} phonon scattering of sp^2 carbon atoms of graphene (G band), respectively. A strong G band such as that can be seen in Fig. 1C 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 Fig. 2C is relatively large at 0.76, which is much lower than that of GO based materials in other literatures [34,35], indicating the low sp^2 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.

Electrochemical impedance spectroscopy (EIS) is an effective method for studying electron transfer resistance of modified electrode surface. In this work, the EIS was used to monitor the fabricating process of the modified electrode. In EIS, the semicircle diameter is equal to the electron transfer resistance and linear partial represents diffusion process. As shown in Fig. 2D, a well-defined semicircle at higher frequencies is obtained at the bare GCE (curve a). As for ZnO TPHS/GCE (curve b), the semicircle decreases significantly, indicating that the ZnO TPHS film on GCE accelerates the electron transfer between the redox probe of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and the electrode surface. For the ZnO TPHS@GO/GCE, the smallest semicircle of EIS curve is obtained, signifying that the conductivity of ZnO TPHS@GO composite is greatly improved. On one hand, the porous frameworks with nano-confined spaces of ZnO TPHS can not only increase the active area accessible to the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ molecules but also provide efficient mass transfer compared with solid counterparts. On the other hand, the intimate contact between GO nanosheets and ZnO TPHS improves the

electrochemical performance significantly.

Chronocoulometry was used to compare the effective surface area (A) of bare GCE (curve a), ZnO TPHS/GCE (curve b) and ZnO TPHS@GO/GCE (curve c) in 0.1 mM $K_3[Fe(CN)_6]$ solution (Fig. 3A) by using the Anson equation [36]:

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2} + Q_{dl} + Q_{ads} \quad (2)$$

where n is the electron transfer number, F is Faraday constant, c is the concentration of $K_3[Fe(CN)_6]$ probe molecule, D is the standard diffusion coefficient (here, $D = 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at room temperature), Q_{dl} is double layer charge which can be eliminated by background subtraction, Q_{ads} is the Faradic charge, and other symbols have their usual meanings. As shown in Fig. 3B, the plots of charge (Q) against $t^{1/2}$ have good linear relationships for the oxidation reactions of $K_3[Fe(CN)_6]$ on bare GCE (curve a'), ZnO TPHS/GCE (curve b') and ZnO TPHS@GO/GCE (curve c'). From the slope of equation (2), the values of A are calculated as 0.076, 0.206 and 0.270 cm^2 for bare GCE, ZnO TPHS/GCE and ZnO TPHS@GO/GCE, respectively. The obvious increase of electrode effective surface area after modification with ZnO TPHS@GO composite comes from the rich porosity of the shells and interior cavities of ZnO TPHS, coupled with the ultrathin nanosheets of GO. Thereafter, the adsorption capacity for analytes and detection sensitivity will enhance.

3.2. Electrochemical behaviors of TBHQ and BHA

The cyclic voltammetric responses for each of the electrodes towards 50 μM TBHQ and BHA were checked in pH 3.0 citric acid- Na_2HPO_4 buffer at a scan rate of 100 mV s^{-1} . For TBHQ, weak oxidation wave at 0.43 V and reduction wave at -0.033 V appear on bare GCE (Fig. 4A, curve a). When the ZnO TPHS/GCE is used, the redox peak currents have a certain increase (Fig. 4A, curve b). For the ZnO TPHS@GO/GCE (Fig.

4A, curve c), the redox peak currents are further improved, of which the oxidation peak current is about 2.47-fold and 3.99-fold higher than that of ZnO TPHS/GCE and bare GCE. And the peak-to-peak separation (ΔE_p) of 0.37 V has significant decrease compared to that on bare GCE. The similar results for the oxidation of BHA at different electrodes are also obtained. Compared with bare GCE (Fig. 4B, curve a) and ZnO TPHS/GCE (Fig. 4B, curve b), the oxidation peak current obtained at ZnO TPHS@GO/GCE is much larger under the same experimental condition (Fig. 4B, curve c), of which the oxidation peak current is about 1.39-fold and 2.46-fold higher than that of ZnO TPHS/GCE and bare GCE, respectively. Furthermore, the oxidation peak potential of BHA on ZnO TPHS@GO/GCE shifts negatively as compared to a bare GCE, indicating greatly promoted charge transfer reaction of BHA on the nanocomposite film. Moreover, the cyclic voltammetric curves of ZnO TPHS@GO/GCE in pH 3.0 citric acid- Na_2HPO_4 buffer are featureless (Fig. 4, curve d), so the oxidation peaks at 0.37 and 0.55 V can be used as the detection signals for TBHQ and BHA, respectively. Importantly, it can be concluded it is possible to determine TBHQ and BHA simultaneously at the ZnO TPHS@GO/GCE because the oxidation peaks of these two species can be separated.

In order to study the reliability of the proposed sensor for simultaneous determination of TBHQ and BHA, SWV was used owing to its high sensitivity and resolution for measuring trace concentrations of analytes. Fig. 5 shows the SWVs of a mixture solution of 34 μM TBHQ and 5.0 μM BHA at different electrodes. On the bare GCE, small broad anodic peaks located at 0.40 and 0.57 V were observed for the oxidation of TBHQ and BHA, respectively (curve a). The anodic peak currents are much improved for ZnO TPHS/GCE (curve b). However, the ZnO TPHS@GO composite exhibits two well-defined and remarkable anodic peaks with greatly

enhanced currents at 0.37 and 0.52 V for TBHQ and BHA, respectively (curve c). The separation anodic peak potential between TBHQ and BHA is 150 mV. The high selectivity and sensitivity obtained using the proposed sensor may be attributed to the following three reasons: (1) the porous structure of ZnO THPS with abundant cavities can make the antioxidant molecules stay longer in the vicinity of the catalyst surface, indicating highly frequent interaction between the antioxidant molecules and electrode surface. (2) The high volume and void space of ZnO THPS allow for better accommodation of volume changes during electrochemical reaction processes, resulting in better structure stability. (3) The intimate contact between ZnO TPHS and GO nanosheets makes electronic interaction possible and is important for the improvement of electrical conductivity. In addition, the SWV response of ZnO TPHS@GO/GCE in the absence of TBHQ and BHA is shown as curve d, it is featureless and no oxidation peaks appear, revealing that the observed anodic peaks are caused by the oxidation of TBHQ and BHA.

The electrochemical oxidation behaviors of 15 μ M TBHQ and 3.0 μ M BHA in many kinds of media including 0.1 M HClO₄, HCl, H₂SO₄, NaOH, citric acid–Na₂HPO₄ buffer (pH 2.2–8.0), Britton–Robinson buffer (pH 1.81–11.58), boric acid–borax buffer (pH 7.4–9.0), acetate buffer (pH 2.6–5.0), carbonate buffer (pH 8.77–10.83), and phosphate buffer (pH 5.8–8.0) were compared by SWV. The excellent oxidation response was obtained in pH 3.0 citric acid–Na₂HPO₄ buffer because the peak current was the highest and the shape of peak was better. As a result, pH 3.0 citric acid–Na₂HPO₄ buffer was chosen as the determining medium for TBHQ and BHA.

The effect of amount of ZnO TPHS@GO on the oxidation peak currents of 15 μ M TBHQ and 3.0 μ M BHA was evaluated using SWV. When gradually improving the

amount of ZnO TPHS@GO from 0 to 10 μL , the peak currents of TBHQ and BHA greatly increased. However, the oxidation peak currents of TBHQ and BHA gradually decreased when the ZnO TPHS@GO content increased from 10 to 20 μL . In this work, the best amount of ZnO TPHS@GO was selected as 10 μL .

In electrochemical determination, accumulation is an effective way to improve the determination sensitivity. In this work, the effects of accumulation potential and accumulation time on the oxidation peak currents of TBHQ and BHA were investigated. In order to evaluate the influence of accumulation potential on the determination of TBHQ and BHA, the oxidation peak currents of 15 μM TBHQ and 3.0 μM BHA after 60-s accumulation under different accumulation potentials were measured by SWV. It was found that the oxidation peak currents almost unchanged as shifting accumulation potential from -0.4 to 0 V, so the open-circuit was applied in the following accumulation step. The dependence of the oxidation peak currents of TBHQ and BHA on the accumulation time was further studied. The oxidation peak currents increased greatly within the first 60 s and then leveled off, meaning that the accumulation of TBHQ and BHA at the ZnO TPHS@GO/GCE reached saturation very quickly.

3.3. Electrochemical reaction mechanism of TBHQ and BHA

First of all, the CV responses of 50 μM TBHQ (Fig. 6A) and BHA (Fig. 6B) on ZnO TPHS@GO/GCE in citric acid- Na_2HPO_4 buffer with different pH values were researched. It showed that when the pH value increased from 2.2 to 8.0, the oxidation peak potentials (E_p) of TBHQ and BHA have obvious negative shift, revealing that proton is involved in the electrochemical oxidation of these two antioxidants. The insets of Fig. 6 demonstrate the E_p of TBHQ and BHA as a function of pH value and

the calculated $[\partial E_p/\partial \text{pH}]$ is -58.2 and -52.5 mV pH^{-1} , respectively, indicating equal number of protons and electrons are involved in the oxidation of TBHQ and BHA.

Next, the effects of scan rate (ν , mV s^{-1}) on the oxidation peak currents (I_p , μA) and oxidation peak potentials (E_p , V) of $50 \mu\text{M}$ TBHQ (Fig. 6C) and BHA (Fig. 6D) were also studied by CV on ZnO TPHS@GO/GCE in pH 3.0 citric acid– Na_2HPO_4 buffer. It is found that the I_p increases gradually with increasing ν from 50 to 400 mV s^{-1} according to the regression equations (inset I of Fig. 6C and D): $I_p = 3.4 + 0.017 \nu$ ($r^2 = 0.995$, for TBHQ), and $I_p = 1.2 + 0.018 \nu$ ($r^2 = 0.996$, for BHA). Additionally, the E_p of TBHQ and BHA shifts positively with increasing ν in the range of $50\sim 400 \text{ mV s}^{-1}$ according to the regression equations (inset II of Fig. 6C and D): $E_p = 0.27 + 0.022 \ln \nu$ ($r^2 = 0.999$, for TBHQ), and $E_p = 0.45 + 0.024 \ln \nu$ ($r^2 = 0.998$, for BHA), revealing that the oxidation processes of TBHQ and BHA at the ZnO TPHS@GO/GCE are irreversible adsorption–controlled.

According to Laviron's equation [36], for an adsorption–controlled and totally irreversible electrode process, E_p and ν are defined by the following equation:

$$E_p = E^0 + \frac{RT}{\alpha n F} \ln \frac{RTk^0}{\alpha n F} + \frac{RT}{\alpha n F} \ln \nu \quad (3)$$

where α is the transfer coefficient, k^0 is the standard rate constant of the reaction, n is the electron transfer number, and E^0 is the formal potential. Other symbols have their usual significance. Therefore, the values of αn for TBHQ and BHA can be easily achieved from equation (3) as 1.17 and 1.07 , respectively. Generally, α is assumed as 0.5 in the totally irreversible electron process. Hence, two electrons are involved in the electrochemical oxidation of TBHQ and BHA. As stated above, the number of protons and electrons taking part in the electrochemical reaction is $1:1$, so the possible electrochemical mechanism for TBHQ and BHA at ZnO HTPHS@GO/GCE can be

assumed as Scheme 2.

3.4. Simultaneous determination of TBHQ and BHA

To study the selectivity of the fabricated sensor, the response currents of ZnO HTPHS@GO electrode toward some organic and inorganic species in the presence of 5.0 μM TBHQ and BHA were conducted. The results show that 2000 times of K^+ , NO_3^- , Cl^- , Na^+ , Zn^{2+} , Ca^{2+} , Fe^{3+} , Cu^{2+} , sucrose, citric acid, glucose, tartaric acid, glycine; 1500 times of Mg^{2+} , SO_4^{2-} , Al^{3+} ; 500 times of 4-nitrophenol, 4-chlorophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, phenol; 50 times of uric acid, ascorbic acid; 5 times of 4-aminobenzoic acid, 4-hydroxybenzoic acid; 2 times of butylated hydroxytoluene have little interference to the measure of TBHQ and BHA (signal change $< 8\%$). Based on the results, it is concluded that the sensor is free from interferences of a large quantity of foreign species.

The reproducibility and repeatability of this sensor were tested by detecting the analytical signals for 10 times at 10 different ZnO TPHS@GO/GCEs (constructed in 10 different days) in pH 3.0 citric acid- Na_2HPO_4 buffer containing 15 μM TBHQ and 3.0 μM BHA. The relative standard deviations (RSDs) for 10 replicate determinations using one sensor in a day were 2.6 and 3.1% for TBHQ and BHA, respectively. Additionally, the RSD values using 10 different sensors constructed in 10 different days were 3.3 and 3.6% for TBHQ and BHA, respectively, confirming the excellent reproducibility and repeatability of the sensor.

Under the optimized experimental conditions, the SWV was applied for simultaneous analysis of different concentrations of TBHQ and BHA. To evaluate this, several binary mixtures of the two antioxidants were prepared, in which the concentration of one antioxidant changed gradually, whereas the concentration of the

other antioxidant remained constant. Square wave voltammograms of these solutions were recorded, as shown in Fig. 7. The obtained results show that the peak current of TBHQ increases linearly with the increase of its concentration in the range of 0.80–65 μM (inset of Fig. 7A), while the responses of 3.0 μM BHA are practically unaffected (Fig. 7A). Similarly, by keeping the TBHQ concentration constant (43 μM), the increase in the peak current for BHA is linear with its concentration in the range of 0.30–60 μM (inset of Fig. 7B), while the anodic peak currents for TBHQ do not change (Fig. 7B). Therefore, it can be concluded that this sensor is suitable for the simultaneous determination of TBHQ and BHA because the oxidation peaks of these two antioxidants are clearly independent from each other. In addition, the detection limit ($S/N = 3$) for TBHQ and BHA is estimated to be 0.137 and 0.0488 μM , respectively, which is much lower than the guideline values in food samples given by the European Union. And compared to the previous electrochemical sensors for the simultaneous determination of TBHQ and BHA, a better performance is observed here (Table 1).

3.5. Practical application

In an attempt to verify the utility of this sensor, the determination of TBHQ and BHA in four edible vegetable oil real samples was performed by the standard addition method. The prepared sample (100 μL) was added to 5.0 mL pH 3.0 citric acid– Na_2HPO_4 buffer in an electrochemical cell. SWV curves were recorded between 0 and 0.8 V after 60-s accumulation under open-circuit (Fig. 8, curve a). Table 2 shows the content of TBHQ and BHA in the four vegetable oil samples, which underwent six parallel measurements. The RSD is below 4%, implying the excellent reproducibility of this sensor in real samples determination. In order to ascertain the

precision of the results, certain amounts of TBHQ and BHA standard solutions were further added into the above pretreated samples and were then detected using this sensor (Fig. 8, curve b). As shown in Table 2, the recoveries of the spiked samples ranging between 95.7 and 106% are satisfactory, revealing that the prepared sensor can be efficiently used to provide results for determination of TBHQ and BHA in real samples.

Furthermore, the results for the determination of TBHQ and BHA in vegetable oil samples obtained by this sensor was compared with that obtained by the published HPLC method using Student's t -test and variance ratio F -test (Table 2). It can be seen that no significant difference exists between the performances of the two methods because the t values for both TBHQ and BHA in these four vegetable oil samples are below the theoretical value of t (2.57, $P = 0.95$), and the F values of them are below 5.05 ($f = 5$, $P = 0.95$). Therefore, the results from this sensor and HPLC are in good agreement, indicative of good accuracy.

4. Conclusion

In summary, triple-shelled porous hollow ZnO spheres (ZnO TPHS) with monodispersed characteristic and controllable diameter were fabricated through an efficient and simple multiple-interface transformation strategy. The number of the shells of the ZnO TPHS could be accurately controlled by controlling the temperature gradient processes. In addition, graphene oxide (GO) nanosheets were successfully wrapped outside the ZnO TPHS, and the composite possessed high specific surface area, desirable pore volume, abundant cavities and increased diffusion of electrons. The study demonstrated that the ZnO TPHS@GO composite greatly affected the final electrochemical properties of glassy carbon electrode, which exhibited as a good

platform for not only greatly enhancing the independent current responses of the oxidation of tert-butylhydroquinone (TBHQ) and butylated hydroxyanisole (BHA), but also decreasing the overpotentials of these antioxidants. Therefore, the proposed ZnO TPHS@GO sensor was applicable for simultaneous determination of TBHQ and BHA. Furthermore, the sensor showed good selectivity, high reproducibility and repeatability, wide linear concentration range, low detection limit, and its application in the detection of TBHQ and BHA in real vegetable oil samples was successful. It is believed that the current research can provide an effective strategy to design better electrode materials for electrochemical sensors.

Acknowledgments

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Biographies

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Figure captions

Scheme 1. Schematic representation of the fabrication of ZnO TPHS@GO modified GCE.

Scheme 2. Probable mechanism for the electrochemical oxidation of TBHQ and BHA.

Fig. 1. SEM (A,B,E) and TEM (C,D,F) images of ZnO TPHS (A–D) and ZnO TPHS@GO (E,F).

Fig. 2. (A–C) EDX elemental analysis spectrum, powder XRD and Raman spectrum of ZnO TPHS@GO. (D) Impedance spectrum for the response of (a) bare GCE, (b) ZnO TPHS/GCE and (c) ZnO TPHS@GO/GCE towards 5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution and 0.1 M KCl.

Fig. 3. Chronocoulometry curves of bare GCE (a), ZnO TPHS/GCE (b) and ZnO TPHS@GO/GCE (c) in 0.1 mM $K_3Fe(CN)_6$ solution containing 1.0 M KCl. Inset: plots of Q vs. $t^{1/2}$ on bare GCE (a'), ZnO TPHS/GCE (b') and ZnO TPHS@GO/GCE (c').

Fig. 4. Cyclic voltammograms of (a) bare GCE, (b) ZnO TPHS/GCE and (c) ZnO TPHS@GO/GCE in the presence of 50 μ M TBHQ (A) or 50 μ M BHA (B) in pH 3.0 citric acid– Na_2HPO_4 buffer. Scan rate: 100 mV s⁻¹. Curve d corresponds to the CV curve of ZnO TPHS@GO/GCE in pH 3.0 citric acid– Na_2HPO_4 buffer.

Fig. 5. SWV curves of TBHQ and BHA in pH 3.0 citric acid–Na₂HPO₄ buffer. (a–c) 34 μ M TBHQ and 5.0 μ M BHA on bare GCE, ZnO TPHS/GCE and ZnO TPHS@GO/GCE, respectively. (d) 0 μ M TBHQ and BHA on ZnO TPHS@GO/GCE. Accumulation was performed under open–circuit for 60 s.

Fig. 6. (A and B) CV curves of 50 μ M TBHQ and BHA on ZnO TPHS@GO/GCE in citric acid–Na₂HPO₄ buffer with different pH values of 2.2 (a), 3.0 (b), 3.8 (c), 5.0 (d), 6.0 (e), 7.0 (f) and 8.0 (g). Scan rate: 100 mV s^{–1}. Inset: plot of E_p vs. pH value. (C and D) CV curves of 50 μ M TBHQ and BHA on ZnO TPHS@GO/GCE in pH 3.0 citric acid–Na₂HPO₄ buffer with different scan rates of 50 (h), 100 (i), 150 (j), 200 (k), 250 (l), 350 (m) and 400 (n) mV s^{–1}. Insets: plots of I_p vs. ν (I) and E_p vs. $\ln \nu$ (II).

Fig. 7. SWVs at ZnO TPHS@GO/GCE in (A) 3.0 μ M BHA and different concentrations of TBHQ: 0.8 (a), 3.0 (b), 8.0 (c), 15 (d), 25 (e), 30 (f), 45 (g), 55 (h), 60 (i) and 65 (j) μ M, and (B) 43 μ M TBHQ and different concentrations of BHA: 0.3 (k), 3.0 (l), 8.0 (m), 15 (n), 20 (o), 30 (p), 40 (q), 50 (r) and 60 (s) μ M. The insets show the calibration plots of TBHQ and BHA vs. peak current. Other conditions are as in Fig. 5.

Fig. 8. SWV curves of this sensor in peanut oil (A), soybean oil (B), sesame oil (C), colza oil (D) samples before (a) and after (b) the addition of TBHQ and BHA standard solution.

Table 1

Comparison of various electrochemical sensors for the simultaneous determination of TBHQ and BHA.

Modified electrode	Analyte	Linear range (μM)	Limit of detection (μM)	Ref.
GCE	TBHQ	2.02–1010	0.23	16
	BHA	2.34–1170	0.18	
Carbon nanotube/screen printed electrode	TBHQ	1–10	0.487	17
	BHA	1–10	0.518	
Multi-walled carbon nanotube/screen-printed electrode	TBHQ	0.5–10	0.34	18
	BHA	0.5–10	0.176	
Nickel phthalocyanine/polypyrrole electrode	TBHQ	20–140 and 120–220	7.4	19
	BHA	200–1000	104	
Gold nanoparticles/GCE	TBHQ	1.2–17	0.475	20
	BHA	0.55–8.3	0.216	
Platinum microelectrode	TBHQ	50–1000	—	21
	BHA	60–1100	—	
Au nanoparticles–electrochemical reduced graphene oxide/GCE	TBHQ	0.60–42.1	0.30	22
	BHA	0.56–55.6	0.23	
Zn TPHS@GO/GCE	TBHQ	0.80–65	0.137	This work
	BHA	0.30–60	0.0488	

Table 2

Detection and recovery of TBHQ and BHA in different vegetable oil samples.

Sample	Analyte	This sensor (μM)	RSD (%)	Added (μM)	Found (μM)	Recovery (%)	HPLC (μM)	t value	F value
Peanut	TBHQ	—	—	3.00	2.91	97.0	—	—	—
oil	BHA	1.08	1.1	3.00	4.16	102	1.12	0.087	2.31
Soybean	TBHQ	2.02	2.7	5.00	6.72	95.7	2.05	0.14	2.55
oil	BHA	1.26	3.6	5.00	6.25	99.8	1.22	0.13	2.29
Sesame	TBHQ	—	—	3.00	2.87	95.7	—	—	—
oil	BHA	1.29	3.7	3.00	4.14	96.5	1.31	0.17	1.33
Colza	TBHQ	1.16	3.3	10.00	11.30	101	1.13	0.18	1.98
oil	BHA	—	—	10.00	10.61	106	—	—	—

Scheme 1

Scheme 2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Biographies

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