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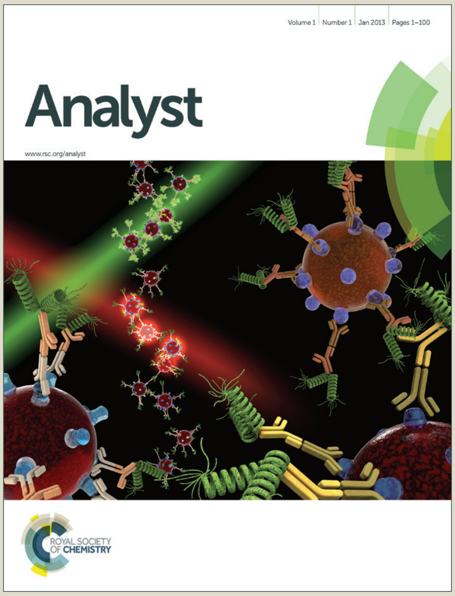

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PAPER

Voltammetric determination of TBHQ at glassy carbon electrode surface activated by in-situ chemical oxidation †

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this article, bare glassy carbon electrode (GCE) surface was directly activated by a simple in-situ chemical method, which was characterized by scanning electron microscope (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectra (EIS). Based on these results, it was found that oxygen-containing functional groups at the modified GCE surface were enhanced with a low damage to the surface state. Hence, the modified GCE exhibited an excellent performance, such as the negatively charged surface, good reproducibility and high selectivity. The resulting electrode was applied as a sensitive sensor for detection of antioxidant tertiary butyl hydroquinone (TBHQ), and a good linear relationship was obtained between oxidation peak current and concentration in a broad range of 1.0 µM - 1.1 mM, with detection limits of 67 nM (S/N=3) by DPV. Electrochemical parameters of TBHQ on the resulted GCE were also investigated, suggesting that the modified GCE could promote electron transfer kinetics towards the electrochemical reaction of TBHQ. Besides, the present method was used for determination of TBHQ in jatropha biodiesel with recovery ranging from 95.2% to 103.2%.

Introduction

Owing to excellent physical and chemical properties, glassy carbon electrodes have been widely used in electroanalytical chemistry.[1] As known, electrochemical behaviours of GCE are associated with the composition and structure of the surface. However, the bare GCE is low-activity for some reactions, because of the poor surface state of the electrode. In order to improve the performance of the surface of electrodes, various surface treatments have been studied to date, such as mechanical polishing,[2, 3] heating,[4] electrochemical oxidation,[5, 6] laser activation,[7] exposure to UV generated ozone[8] and photocatalytic pretreatment.[9] Among these methods, electrochemical oxidation is the most extensively studied one due to its good reproducibility and easy operation,[10] and the electron transfer rate or adsorptive behavior of the GCE for some electroactive analytes is largely increased with oxidative treatments. However, the chemical oxidation method has rarely been reported so far because of the stability of the glassy carbon.

To our knowledge, food preservation is of great significance in daily life. One important way is to add various synthetic antioxidants, such as propyl (PG), octyl (OG) and dodecyl (DG), butylated hydroxytoluene (BHT), butyl hydroxyanisole (BHA) and tertiary butyl hydroquinone (TBHQ). TBHQ is one of the most common synthetic phenolic antioxidants owing to its chemical stability, low cost and availability as an oil antioxidant. According to the recommendations of international organizations, the usage of synthetic antioxidants is regulated by legal authorities in a limited number of food, with maximum limits in each case or association,[11] so it's essential to develop an analytical method for monitoring the excessive use of permitted antioxidants and their degenerative products. Analytical methods for determining TBHQ, generally used in oil and food samples, have been widely reported over the past few decades,[12-17] such as high-performance liquid chromatography (HPLC),[18-21] gas chromatography (GC),[22-24] capillary electrophoresis, micellar electrokinetic capillary chromatography[25-27] and fourier transform infrared (FTIR) spectroscopy.[28] However, the instruments that used by these methods are quite expensive or require a rather complicated preparation of sample prior to the analysis and inappropriateness for field use. Electrochemical approaches are simple, cheap and effective.[29] A variety of voltammetric techniques have been used for the determination of TBHQ in different samples including biodiesel.[30-34]

Biodiesel is a renewable and green fuel derived from oils or fats with alcohol and alkaline as catalyst. It has many advantages over mineral diesel such as higher flash point, better lubricity and lower particulate matter emissions. Nevertheless, biodiesel is highly prone to oxidation over a period of storage. The oxidation chain reaction is usually initiated due to the presence of significant amount of fatty acids with double bond, when biodiesel is exposed to air, heat, light, and metallic contaminants, and this fuel instability can bring about sediments and gum formation. The degraded biofuel in engine can lead to operational problems like filter clogging and injector fouling.[35] Therefore, antioxidant compounds are required to improve the inoxidizablity of biodiesel. Among all the antioxidant compounds, the antioxidant property of TBHQ was superior to other antioxidants resulting from its molecular structure.[36] Recently, a variety of

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electrochemical methods for determination of TBHQ have been described.[37, 38] However, the method with our modified GCE has not been reported yet.

In this work, a bare GCE was directly treated by an in-situ chemical method. The merits of the in-situ chemical method are similar to those of electrochemical treatment, such as high electron transfer rate, direct modification without complex pretreatment, preventing abscission of active ingredients from the surface resulting from drop-casting. For two methods, the most significant change on the GCE surface is the increasement of oxygen-containing functional groups. According to XPS results of the electrochemically activated GCE in literature,[39] the oxidizing level of electrochemical method was higher than that of the chemical method in terms of C/O ratio. However, the chemical method has a lower oxidative damage to the electrode surface, which could make the electrode repeatedly modified after a simple polishing process. Electrochemical behaviors of some electroactive materials on the unmodified and modified GCE were investigated, showing that the modified GCE exhibited a good performance like the electrode modified by graphene oxide with a covalent coupling method, deducing that the surface of the resulting electrode could present a negative charge characteristic. The resulting GCE was applied for determination of the TBHQ in 5% (v/v) methanol–water solution with 0.1 M $HClO_4$ by DPV based on its electrochemical oxidation. Finally, the prepared sensor was used to detect TBHQ in jatropha biodiesel with the standard addition method, and the recovery was within a reasonable range.

Experimental

Apparatus

Elemental composition analysis was measured by X-ray photoelectron spectroscopy (XPS, Thermo V4105). Scanning electron microscopy (SEM) images of the unmodified and modified GCE were taken on a Hitachi S-4800 field-emission SEM system. AFM results were obtained from a Veeco Multimode Nanoscope IIIa controller in noncontact mode. All the electrochemical measurements were performed on a potentiostat/galvanostat Autolab (PGSTAT 30/302, Netherlands) electrochemical analyzer system using the GPES software. A conventional three electrode cell was used: a bare or modified GCE with a diameter of 3 mm as the working electrode, an Ag/AgCl (saturated by KCl) as auxiliary electrode and a Pt foil as counter electrode and all the experiments were conducted in the presence of dissolved oxygen and at room temperature. In this research, the experiment was carried out by DPV from 0.20 to 0.70 V and the DPV conditions were optimized as follows: step potential, 0.0025 V; modulation amplitude, 0.05 V; modulation time, 0.05 s; interval time, 0.5 s; equilibration time, 5 s.

Material and Reagents

Potassium persulfate ($K_2S_2O_8$) was obtained from Meilin Industry and Trade Co., Ltd. (Tianjin, China). Concentrated sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), phosphorus pentoxide (P_2O_5) and hydrogen peroxide (30%, w/w in water) were purchased from Kelong Chemical Reagent Company (Chengdu, China). Tertiary butyl hydroquinone (TBHQ, 97% purity, prepared in CH_3OH) was purchased from TCL Development Co., Ltd. (Shanghai, China). TBHQ standard working solutions were prepared by diluting suitable amounts of a standard stock solution in methanol at concentration of 0.1M, 0.01M, 0.001M, and all samples were kept refrigerated before use. Jatropha antioxidant-free biodiesel was obtained from a chemical laboratory of Sichuan University. All other reagents employed were of analytical grade and double distilled water was used throughout the experiments. DPVs for TBHQ were recorded in the optimized conditions in the supporting electrolytes of 5% (v/v) methanol–water solution with 0.1 M $HClO_4$.[40]

Preparation of the modified GCE

Prior to oxidation of the bare electrode, the GCE was in turn polished with 0.3 μm and 0.05 μm alumina powders, and then successively sonicated in 1:1 (v/v) HNO_3–water solution, 1:1 (v/v) ethanol–water solution and double distilled water for 3 minutes. The pretreated bare GCE was oxidized by a method similar to the preparation method of graphene oxide.[41] Different from the method in literature, the reactant graphite powder was replaced by a bare GCE. The reaction time was kept at 80°C for 24 h in the preoxidation step. Next, in the second oxidation step, the temperature was kept at 35 °C for 12 h, and the reaction time was extended in order to ensure the bare GCE fully oxidized. The resulting GCE was copious ultrasonic washed by H_2O_2 (3%) and double distilled water for a few minutes. At last, the modified GCE was gently blown under a nitrogen stream.

Sample preparation

Samples of antioxidant-free biodiesel were spiked with TBHQ to a final concentration of 2000 ppb, 4000 ppb and 8000 ppb, followed by vigorous mechanical agitation. Then 5 mL of the spiked solution was mixed with 10 mL of methanol. After shaking for 5 min, this mixture was centrifuged at 5000 rpm for 20 min and the supernatant was collected. The extraction was repeated once with methanol. The extracts were collected together, concentrated to a final volume of 5mL and kept refrigerated for analysis.[33]

Results and Discussion

Characterization of the modified GCE

The surface roughness would be increased when a bare GCE was treated by an oxidation process, which was characterized by SEM and AFM. Based on our SEM results, it could be easily found that the unmodified GCE did not show any major features on the surface except a little dust and some striations from the polishing at the magnifications ranging from 100× to 5000 × with beam energy of 5 Kev, which was the same with the modified GCE, assuming that the chemical oxidation was a minor destruction process to the surface of electrodes, and it was further confirmed by the similar results of electrochemical responses to 5.0 mM $[Fe(CN)_6]^{3-/4-}$ on the unmodified and modified GCEs by fully polishment (Fig. S2B). Next, AFM measurement was employed to reflect the roughness of the electrode surface. AFM images were shown in Figure 1. The bare GCE surface (Fig. 1A) was relatively flat and smooth and the average roughness (R_a) was 2.072 nm while a lot of bumps were observed at the modified GCE surface (Fig. 1B) and its R_a was 4.542 nm. It was clearly indicated that significant changes in the electrode interface of the

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glassy carbon electrode were generated by the chemical oxidation.

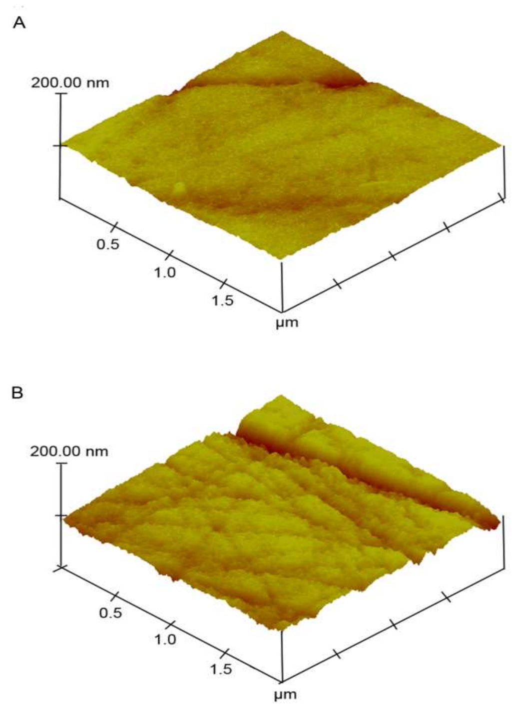

Fig. 1 AFM images of (A) the unmodified GCE and (B) modified GCE

Elemental composition results were obtained by XPS measurements. As seen in Fig. 2A and 2B, the atomic C/O ratio of the resulted GCE (Fig. 2B) was calculated to 4.09, which was lower than that (5.22) of the bare GCE (Fig. 2A). However, the result was higher than that (2.78) of the electrochemically activated GCE in literature,[39] which indicated that the chemical oxidation had a little weaker oxidation capability. The C1s region of the modified GCE (Fig. 2D) showed carbons presented in four different chemical environments, corresponding to C=C at 284.3 eV (curve a), C-C/C-H at 284.2 eV (curve b), C-OH at 285.1 eV (curve c) and C=O/-COOH at 288.3 eV (curve d), and the C=O/-COOH was not found in Fig. 2C. Amount of all the chemical bonds were calculated by XPSPEAK41. Compared to the bare GCE, the C-OH and C=O/-COOH on the modified GCE had an increase of 4.44% and 19.11%, respectively, while C=C reduced by 23.53%. That is, the loss of C=C was completely converted to C-OH and C=O (-COOH). The higher degree of surface oxidation would result in more surface defects, which could be benefit to the increasement of active sites at the GCE surface, further causing adsorption of some electroactive substance to the surface of electrode to be improved.

Electrochemistry characteristics of electroactive compounds

The resulting GCE was characterized by electrochemical technologies. From the electrochemical impedance spectroscopy (EIS) showed in Fig. S3, compared to the bare GCE (curve a), the charge transfer resistance of the modified GCE was largely increased by the first oxidation (curve b), which demonstrated the bare electrode had been initially oxidized, when the GCE showed poor activity to TBHQ. In the second oxidation, the resistance of resulting GCE rose sequentially, suggesting that the GCE was further oxidized. All the results revealed that the bare GCE was successfully oxidized by this method. Next, the adsorption of some electroactive compounds to the surface of the modified GCE was investigated, such as $[Fe(CN)_6]^{3-/4-}$, ascorbic acid (AA), dopamine (DA), catechol (CC) and hydroquinone (HQ). According to the electrochemical behaviors of these compounds, it was well suggested that the modified electrode would repel anionic species while would attract cationic species or quinines, which was consistent with results of the literature.[42] Compared to the bare GCE, the background current of these investigated compounds at the modified GCE was apparently large, that is because the oxygen-rich surface of resulting GCE accelerated electron transfer kinetics. As seen in Fig. 3A and Fig. 3B, the redox peaks of $[Fe(CN)_6]^{3-/4-}$ (Fig. 3A, curve b) and AA (Fig. 3B, curve b) on the resulting GCE were significantly suppressed in comparision with the unmodified GCE (curve a). In contrast, when the resulting GCE was used, redox response of DA was largely increased (Fig. 3C, curve b). These changes could be attributed to electrostatic interaction between these electroactive compounds and the electrode. Proposed mechanism was put forward that AA and $[Fe(CN)_6]^{3-/4-}$ were negatively charged while DA was positively charged under the measured conditions (pH > 5). Comprehensive analysis of their electrochemical behaviors, a conclusion was drawn that the surface of the modified GCE could present a negative-charge characteristic. Based on these results, the experiment would be carried out about

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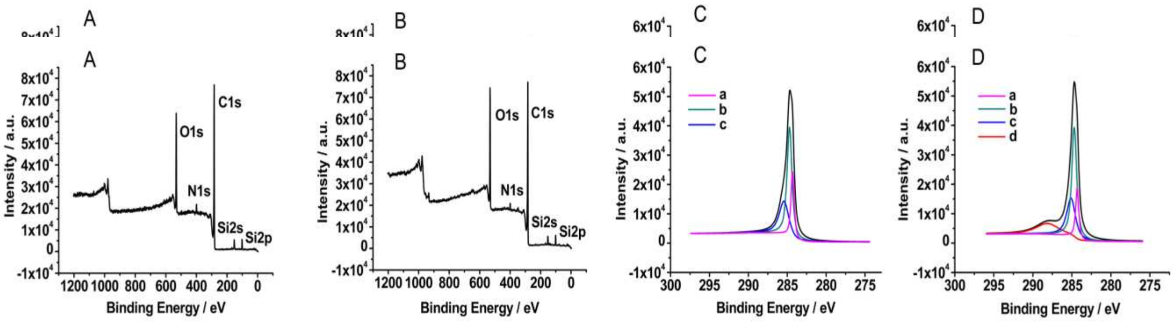

Fig. 2 XPS survey spectrum of (A, C) the unmodified GCE and (B, D) modified GCE; (A, B) Full spectrum and (C, D) C1s spectrum. (a) C=C; (b) C-C/C-H; (c) C-OH; (d) C=O/-COOH.

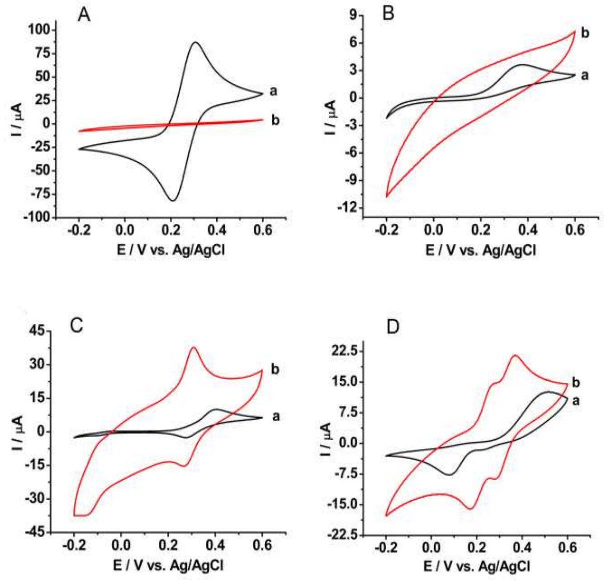

Fig. 3 (A) Cyclic voltammograms (CVs) of 5.0 mM [Fe(CN)6]$^{3-/4-}$ (1:1) with 0.1 M KCl for (a) the bare GCE and (b) modified GCE at 0.05 V s^{-1}; (B) CVs of 0.4 mM AA, (C) 0.4 mM DA and (D) 0.4 mM CC together with HQ on (a) the bare GCE and (b) resulted GCE in 0.1 M PBS with 0.1M KCl solution (pH=6.55) at a scan rate of 0.05 V s^{-1}.

selective detection of DA in present of AA (Fig. S1). Fig. 3D further showed the resulted GCE had an excellent performance, where two pair of well separated redox peeks of HQ and CC were obtained with using the modified GCE (curve b) while the redox peaks completely overlapped on the bare GCE (curve a), indicating that the modified GCE was used to simultaneously detect HQ and CC. Sorption of phenolics to the activated GCE was greatly enhanced, possibly caused by a combined effect, hydrogen bonding between the -OH of the phenolics and -OH or -COOH groups of the GCE surface and -OH-enhanced π-π interactions between phenolics and the GCE surface.[43] The proposed sorption mechanism was also applicable to TBHQ at the modified GCE, and the electrochemical response of TBHQ on the resulting GCE can be explained as follows (Fig. 4A).

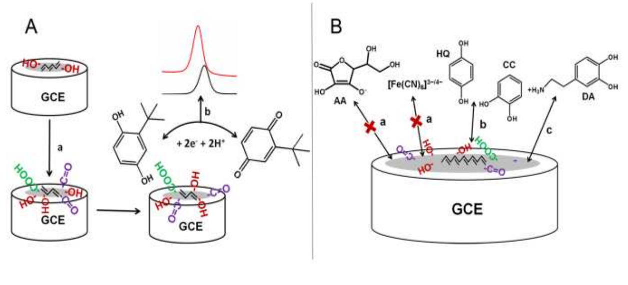

Fig. 4 Proposed models of (A) preparation of the modified GCE and the electrochemistry response of TBHQ on the resulting GCE ((a) in-situ chemical method and (b) electrochemically oxidation) and (B) electrochemical responses of AA, [Fe(CN)$_6$]$^{3-/4-}$, HQ, CC, DA (from left to right) on the surface of the modified GCE ((a) electrostatic repulsion, (b) intermolecular hydrogen bonds combined with π-π stacking and (c) electrostatic attraction coordinated with π-π stacking).

As seen in Fig. 4A, a bare GCE was oxidized by our method, leading to more oxygen-containing function groups and less C=C bonds. When TBHQ was added to the supporting electrolyte, the TBHQ molecules could reach to the surface more easily and produced a stronger electrochemical signal. Interaction mechanism between different electroactive substances and the modified electrode were proposed in Fig. 4B.

Electrochemical determination of TBHQ

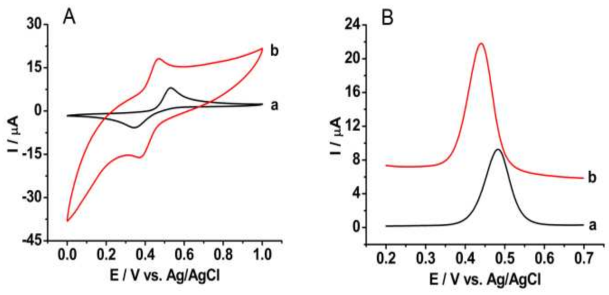

Fig. 5 (A) CVs of 0.4 mM TBHQ on (a) the bare GCE and (b) modified GCE at a scan rate of 0.05 V s^{-1}; (B) DPVs of 0.4 mM TBHQ on (a) the unmodified GCE and (b) modified GCE.

CVs of TBHQ on the bare GCE (curve a) and resulting GCE (curve b) were showed in Fig. 5A, respectively. On the resulting GCE, the redox peak of TBHQ was enhanced together with the background current increasing (Fig. 5A, curve b). The cathode peak potential appeared at ca. 275 mV on the bare GCE (curve a) while the reduction peak potential on the modified GCE positively shifted to 362 mV (curve b), leading to a narrow ΔE_p. Besides, the peak current intensity on the resulting GCE was increased 2.3 times higher than that on the bare GCE. It was also found that the anodic peak potential on the modified (curve b) shifted to more negative values as showed in Fig. 5B. It was assumed that the electrocatalytic activity of surface of the modified GCE in relation with these electrochemical behaviors of TBHQ enhanced the electrochemical reaction. Meanwhile, in the control experiment, a traditional electrochemical anodization method was used to activate a polished GCE. By optimizing oxidation potential and time, the optimized condition was established to 1.8 V for 3 min in 0.1 M sulfuric acid solution, and maximum and stable redox peak current of TBHQ would be obtained. The oxidation peak current of TBHQ would increase 3.3 times than that of the bare GCE with the activated GCE. It was clear that the prepared GCE in this article has a lower adsorption of TBHQ than electrochemically activated GCE. It could be attributed to surface oxygen groups' content. However, from results in Fig. S1, the activated GCE did not exhibit eletronegativity as good as the modified GCE in this article when used to detect the above four eletroactive compounds.

To better understand the electrochemical mechanism of TBHQ on the modified GCE, CV curves of TBHQ at various scan rates were also investigated (Fig. 6). With the increase of scan rates, redox peak currents increased. The anodic and cathodic peak currents were linearly proportional to the square root of scan rates ranging from 0.01 V s^{-1} to 0.5 V s^{-1} (Fig. 6B), and the regression equations were I_{pa} (μA) = 3.993 + 69.354 $v^{1/2}$ ($V^{1/2}$ $s^{-1/2}$) (R^2 = 0.999) and I_{pc} (μA) = -1.528 – 56.881$v^{1/2}$ ($V^{1/2}$ $s^{-1/2}$) (R^2 = 0.996),

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respectively. This result indicated that the redox process of TBHQ on the modified GCE was a quasi-reversible and diffusion-controlled process in bulk solution.

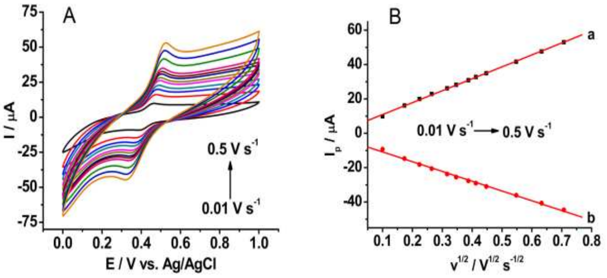

Fig. 6 (A) CVs of 0.4 mM TBHQ on the modified electrode in 5% (v/v) methanol–water solution with 0.1 mol/ L $HClO_4$ at various scan rates: 10, 30, 50, 70, 100, 120, 150, 170, 200, 300, 400, 500 V s^{-1} (from inner to outer), respectively; (B) Liner relationship between peak current and the square root of scan rate ((a) $E_{pa} – v^{1/2}$, (b) $E_{pc} – v^{1/2}$).

For a quasi-reversible electrochemical process, the electron transfer coefficient (α) and the standard electron transfer rate constant (k_s) of TBHQ on the modified electrode were determined according to the following Laviron's equations:[42, 44]

$$E_{pa} = \frac{E^0 + 2.3RT}{(1-\alpha)nF\, log\, v} \tag{1}$$

$$E_{pc} = \frac{E^0 - 2.3RT}{\alpha nF\, log\, v} \tag{2}$$

$$log\, K_s = \alpha\, log(1-\alpha) + (1-\alpha)\, log\, \alpha - log\frac{RT}{nFv} - \frac{(1-\alpha)\alpha nF\Delta E_p}{2.3RT} \tag{3}$$

In these equations, n is the number of electron transferred in reaction (n = 2) and other symbols have their usual meanings. Fig. 7 was the plots of E_p versus log v.

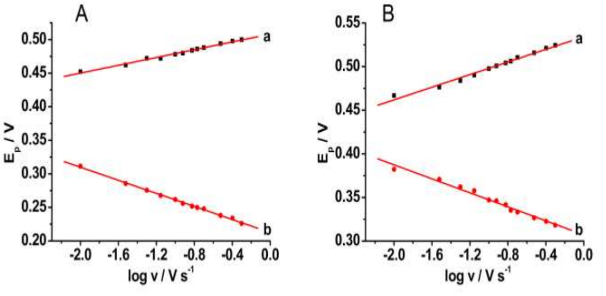

Fig. 7 Liner relationship between E_p and log v of TBHQ on (A) the bare GCE and (B) modified GCE. (a) E_{pa} – log v, (b) E_{pc} – log v.

The linear relationships between the oxidation peak potential (E_{pa}) and the reduction peak potential (E_{pc}) with the logarithm values of v (log v) on the bare GCE were established to E_{pa} (V) = 0.02906 log v (V s^{-1}) + 0.421 (R^2 = 0.985, curve a) and E_{pc} (V) = 0.04869 log v (V s^{-1}) - 0.3586 (R^2 = 0.998, curve b), respectively. The equations of peak potential vs. log v on the modified GCE were established to E_{pa} (V) = 0.0362 log v (V s^{-1}) + 0.4257 (R^2 = 0.985, curve a) and E_{pc} (V) = 0.04017 log v (V s^{-1}) - 0.4277 (R^2 = 0.990, curve b), respectively. From the slope and intercept, the values of α for the unmodified and modified GCE were calculated to 0.49 and 0.59, respectively. Then according to Eq. (3), the values of K_s for the unmodified and modified GCE were calculated to 0.12 s^{-1} and 0.51 s^{-1}, respectively. The result obviously showed that the resulting GCE had a high catalytic capacity to promote electron transfer kinetics toward the electrochemical reaction of TBHQ.

Voltammetric determination of TBHQ

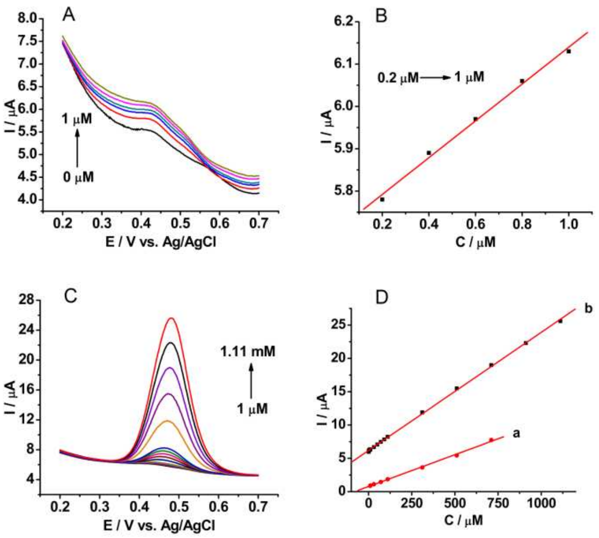

Fig. 8 (A) DPVs of TBHQ with different concentrations in the range of 0.2 μM to 1.0 μM; (B) plots of the peak current vs. the concentration of TBHQ corresponding to Fig. 8A; (C) DPVs of TBHQ with different concentrations ranging from 1.0 μM to 1.1 mM; (D) the linear relationships between peak current and concentration of TBHQ on (a) the bare GCE and (b) modified GCE corresponding to Fig. 8C.

When the modified electrode was employed to detect different concentrations of TBHQ by DPV, the calibration plots were divided two parts (Fig. 8B and Fig. 8D). As seen in Fig. 8A and Fig. 8C, the peak currents enhanced gradually with the adding of TBHQ. From the result of Fig. 8B, it was found that the oxidation peak current of TBHQ presented a linear relationship with the TBHQ concentration ranging from 0.2 μM to 1.0 μM, and the regression equation was I (μA) = 5.705 + 0.437 C (μM) (R^2 = 0.9943). The detection limit was calculated as 64 nM (S/N = 3), which was lower than that of the related report.[45] According to the results of Fig. 8B, the oxidation peak currents were also linearly proportional to different concentrations of TBHQ in the range of 1.0 μM to 1.1 mM (curve b, I (μA) = 6.184 + 0.0177 C (μM), R^2 = 0.9995), while the detection range of the bare GCE was from 7 μM to 0.7 mM (curve a, R^2=0.9974), demonstrating that this modified electrode was superior to the unmodified GCE in analysis of TBHQ in 5% (v/v) methanol–water solution containing 0.1 mol L^{-1} $HClO_4$. Besides, the stability and reproducibility of the sensor were also investigated. The stability of the electrode was checked by performing 30 consecutive measurements with a relative standard deviation (RSD) of 0.36% (Fig. S2A). The reproducibility of the resulted GCE was tested, and the RSD was 3.9% for the same modified GCE fully polished

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after each modification (repeating four times, Fig. S2B), revealing that this method had a good reproducibility.

Interference studies

Some interferences may be generated derived from preparation of biodiesel, such as K^+, Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- and glycerine. These impurities can possibly make interference in the quantitative detection of TBHQ in biodiesel. Therefore, the interferences of these species were conducted with the modified GCE at the optimized condition by DPV for detection of 0.5 mM TBHQ containing 10-fold excess amount of various interfering molecules in 5% (v/v) methanol–water solution with 0.1 M $HClO_4$. In the Table 1, it was found that the oxidation current of TBHQ was not affected by the presence of these compounds. These results suggested that the determination of TBHQ in biodiesel is very reliable.

Table 1 Influence of interferents on the voltammetric responses of 0.5 mM TBHQ.

Interferent	Concentration (mM)[a]	Current Ratios[a,b]
K^+	5	0.97
Na^+	5	0.99
Ca^{2+}	5	0.97
Mg^{2+}	5	0.95
Cl^-	5	0.99
SO_4^{2-}	5	0.99
glycerine	5	1.01

[a] Average value from three determinations

[b] Ratio of currents for mixture of 0.5 mM TBHQ and 5 mM substance compared with 0.5 mM TBHQ only

TBHQ detection in real sample of biodiesel

Table 2 Recoveries of the TBHQ detection in jatropha biodiesel samples.

Sample	TBHQ added ppb(μM)	TBHQ found[a] ppb(μM)	Recovery (%)	RSD[a,b]
1	2000(0.602)	1903(0.573)	95.2	2.3
2	4000(1.204)	3970(1.195)	99.3	1.5
3	8000(2.409)	8254(2.486)	103.2	2.1

[a] Average value from three determinations

[b] RSD was the relative standard deviation of the three measurements by the prepared sensor

Under the optimized conditions, the modified GCE was applied to detect TBHQ in jatropha biodiesel (freshly prepared, free-antioxidants). Biodiesel samples were treated as described in experimental section and 0.5 mL of the extract was added into 10mL of supporting electrolyte in electrolytic cell. For each concentration, three experiments were performed by DPV. The standard addition method was applied and the recovery value was calculated from these results. The recoveries were in the range of 95.2–103.2%, which suggested that the sensor might be used for the determination of TBHQ in real samples.

Conclusions

In this research, an in-situ chemical method was developed to activate the bare GCE. From the results of XPS, SEM, AFM and electrochemical technologies, it was found that the surface roughness was largely increased and the surface contained more oxygen groups and presented a negative-charge characteristic, which could achieve a selective adsorption of some substances. Based on its performance, the modified GCE was applied to detect TBHQ by DPV. The electrochemical parameters such as transfer coefficient (α) and electron transfer rate constant (k_s) of TBHQ on the modified GCE were also investigated, revealing that this modified electrode has a good catalytic ability towards TBHQ. Under the optimized conditions, the liner relationship included two parts with the detection limits of 64 nM. Finally, the proposed method was successfully applied to TBHQ detection in jatropha biodiesel with recovery ranging from 95% to 103.2%.

Acknowledgements

The research was supported by the National Natural Science Foundation of China (No.21377089, No.21177090).

Notes and references

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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