

Electrochemical behavior of tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode

Z. Y. Cai · L. Z. Pei · Y. Yang · Y. Q. Pei · C. G. Fan ·
D. G. Fu

Received: 23 October 2011 / Revised: 6 January 2012 / Accepted: 9 January 2012 / Published online: 28 January 2012
© Springer-Verlag 2012

Abstract The electrochemical behavior of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode has been investigated by cyclic voltammetry (CV). The results show that two pairs of semireversible electrochemical peaks are observed and can be assigned to the process of oxidation–reduction and adsorption–desorption of tartaric acid at the modified glassy carbon electrode, respectively. The intensity of the CV peaks increases linearly with the increase of the content of tartaric acid in the range of 0.01–5 mM and scan rate ranging from 25–200 mV s⁻¹. CuGeO₃ nanowire modified glassy carbon electrode exhibits good detection ability for tartaric acid in neutral solution with the detection limit of 8.9 and 7.7 μM for cvp1 and cvp2, respectively, at a signal-to-noise ratio of 3. The CuGeO₃ nanowire modified glassy carbon electrode has good reproducibility and stability.

Keywords Tartaric acid · CuGeO₃ nanowires · Electrochemical behavior

Introduction

Like other biological molecules, such as cysteine, ascorbic acid, and dopamine from the group of hydrocarboxylic acids, tartaric acid (C₄H₆O₆) is widely used in the food and chemistry industry, pharmacology, and other fields. Therefore, it is great significance of developing convenient, rapid, and facile method for detecting tartaric acid for food, chemistry industry, pharmaceutical quality and safety [1–3]. With the development of the electrochemical (EC) detection technology, the investigation on the electrochemical behavior of different biomolecules at electrodes gives us unprecedented insight into the electrochemistry science which exhibits excellent sensitivity, rapid response, low cost, and good convenience [4–7]. However, only several research groups reported the electrochemical behavior of tartaric acid at different electrodes. For example, electrochemical behavior of tartaric acid at Pt-, Cu-, Ta-, Cu–Hg electrodes, and Cd alloys with Sn, Ni, Hg, and In in aqueous and mixed solution [water mixtures with acetone, ethanol, dimethylformamide (DMF), and pyridine] has been analyzed [1]. Galkwad et al. [8] reported the indirect chemiluminescence determination of tartaric acid with a relative standard deviation (RSD) below about 2%. However, the accurate determination of the concentration of tartaric acid is of considerable importance, but the reliable sensing of tartaric acid using conventional electrodes has been hindered.

Nanowires can be used as the modified electrode materials due to their high surface-to-volume ratio, excellent surface activity, and electrochemical properties [9–11]. In particular, some effort has been devoted to CuGeO₃ nanowires as the electrode modified materials owing to CuGeO₃ nanowires exhibiting good electrochemical detection ability for cysteine with the potential application in electrochemical sensors [12]. Similar to the structure of cysteine, tartaric acid has also

Z. Y. Cai · D. G. Fu
State Key Laboratory of Bioelectronics, School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China

Z. Y. Cai · L. Z. Pei (✉) · Y. Yang · Y. Q. Pei · C. G. Fan
Key Lab of Materials Science and Processing of Anhui Province, School of Materials Science and Engineering, Anhui University of Technology, Ma'anshan, Anhui 243002, People's Republic of China
e-mail: lzpei1977@163.com

L. Z. Pei
e-mail: lzpei@ahut.edu.cn

hydroxyl groups. Therefore, the glassy carbon electrode (GCE) modified with CuGeO_3 nanowires may also exhibit good electrochemical detection ability for tartaric acid, stimulating our research interest for the electrochemical behavior at the conventional glassy carbon electrode modified with CuGeO_3 nanowires for detecting tartaric acid.

In the paper, CuGeO_3 nanowires are used as the glassy carbon electrode modified materials for the electrochemical detection of tartaric acid. The detection range, detection limit, stability, and reproducibility of the CuGeO_3 nanowires modified glassy carbon electrode for detecting tartaric acid are analyzed. And the electrochemical sensing process for tartaric acid is also analyzed.

Experimental

Fabrication of the CuGeO_3 nanowire modified glassy carbon electrode

The CuGeO_3 nanowires were prepared by hydrothermal deposition process which is described elsewhere [13]. The hydrothermal deposition temperature and time are 250 °C and 12 h, respectively. The CuGeO_3 nanowire suspension was prepared by dispersing 10 mg CuGeO_3 nanowires in 10 mL DMF solvent with sufficient ultrasonication for about 1 h until a relatively uniform nanowire suspension was gained. Prior to modification, a GCE (3 mm in diameter) was polished to a mirror with polish paper and alumina pastes of 0.5 μm , and cleaned thoroughly in an ultrasonic cleaner with alcohol and water sequentially. The CuGeO_3 nanowire modified glassy carbon electrode was prepared by coating 10 μL nanowire suspension on the surface of bare electrode which is dried at room temperature in air.

Characterization methods

The sample was observed by scanning electron microscopy (SEM) which was performed using JEOL JSM-6490LV SEM with a 15-kV accelerating voltage. Tartaric acid was purchased from Sinopharm Chemical Reagent Co., Ltd. of China which is analytical grade. EC measurement was performed in a model CHI6046 electrochemical working station. The CuGeO_3 nanowire modified glassy carbon electrode serves as the working electrode, and a platinum plate and a saturated calomel electrode (SCE) serve as the counter electrode and reference electrode, respectively. All potentials in the research are with respect to SCE. Cyclic voltammograms (CVs) were recorded in the potential range of -1.0 to 1.0 V at a potential scan rate of 50 mV s^{-1} in the mixed solution of 0.1 M KCl and tartaric acid with different concentration. All measurements were carried out at room temperature.

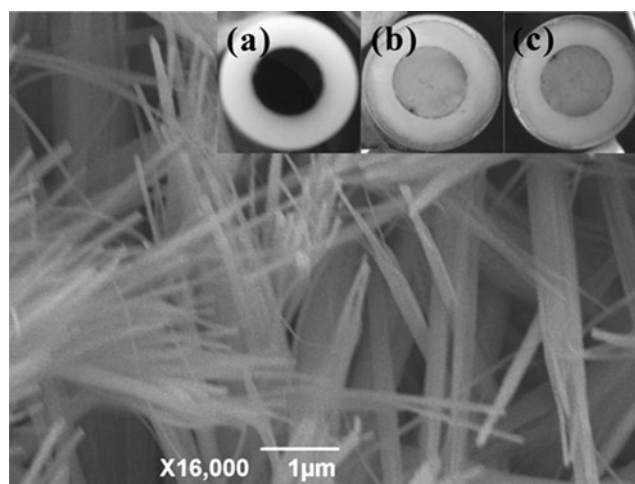


Fig. 1 SEM images of the CuGeO_3 nanowire modified glassy carbon electrode. The insets in the upper right part are the digital images of the surface state of the glassy carbon electrode: bare glassy carbon electrode (a), glassy carbon electrode coated with CuGeO_3 nanowires (b), CuGeO_3 nanowire modified glassy carbon electrode immersed in the mixed solution of 0.1 M KCl and 2 mM tartaric acid after 2 days (c)

Results and discussion

Surface state of the CuGeO_3 nanowire modified glassy carbon electrode

CuGeO_3 nanowires were coated on the surface of the bare glassy carbon electrode using simple dropping method. Figure 1 shows the SEM image of the surface state of the CuGeO_3 nanowire modified glassy carbon electrode. It is observed that the diameter of the CuGeO_3 nanowires is 50

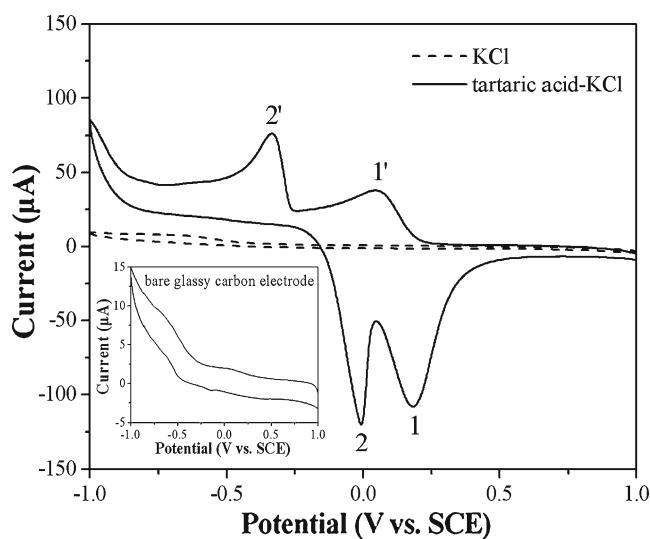
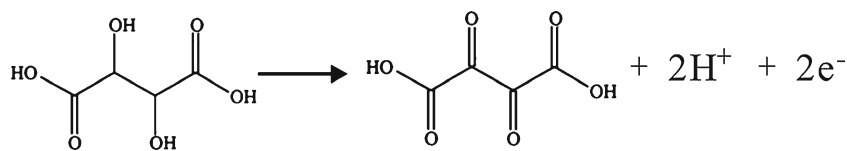


Fig. 2 CVs of the CuGeO_3 nanowire modified glassy carbon electrode in 0.1 M KCl solution in the absence and presence of tartaric acid with the concentration of 2 mM. The inset in the bottom left part is the CV of the bare glassy carbon electrode in 0.1 M KCl and 2 mM tartaric acid solution. Scan rate 50 mV s^{-1}

Scheme 1 The oxidation process of tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode



to 200 nm. The inset of the upper right part of Fig. 1 displays the digital images of the bare glassy carbon electrode, glassy carbon electrode coated with CuGeO₃ nanowires, and CuGeO₃ nanowire modified glassy carbon electrode immersed in the mixed solution of 0.1 KCl and 2 mM tartaric acid after 2 days. It is found that the bare glassy carbon electrode has smooth surface with black color (a in the upper right part of Fig. 1). A dense CuGeO₃ nanowire film can be formed on the surface of the glassy carbon electrode (b in the upper right part of Fig. 1). The dense CuGeO₃ nanowire film can still exist in the surface of the glassy carbon electrode (see c in the upper right part of Fig. 1). The result shows that only dipping and drying can give a solid coating on the electrode surface. Therefore, the substrate of the modified CuGeO₃ nanowires glassy carbon electrode may exhibit slight effect on the electrochemical behavior of the tartaric acid.

Electrochemical behavior of tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode

The electrochemical behavior of tartaric acid at the bare glassy carbon electrode and CuGeO₃ nanowire modified glassy carbon electrode was analyzed by CV in 0.1 M KCl solution and the mixed solution of 0.1 M KCl and 2 mM tartaric acid (Fig. 2). No CV peaks are observed from the CV curve of the CuGeO₃ nanowire modified glassy carbon electrode in 0.1 M KCl solution without tartaric acid. Similarly to the electrochemical behavior of the CuGeO₃ nanowire modified glassy carbon electrode in 0.1 M KCl solution without tartaric acid, no CV peaks are also observed from the CV curve of tartaric acid at the bare glassy carbon electrode in 0.1 M KCl solution (inset in the bottom left part of Fig. 2). The result shows that CuGeO₃ nanowires and bare glassy carbon electrode have no electrochemical activity in the potential range of -1 to +1 V. The electrochemical behaviors are very different in 0.1 M KCl with and without tartaric acid. Two anodic CV peaks (cvp1, cvp2) are located at 0.182 and 0.016 V, and two cathodic peaks (cvp1', cvp2') are located at 0.045 and -0.334 V, respectively. The anodic and cathodic CV peaks are only observed in 0.1 M KCl and 2 mM tartaric acid solution at the CuGeO₃ nanowire

modified electrode. Therefore, it is considered that these CV peaks are caused by the tartaric acid. The CuGeO₃ nanowires on glassy carbon electrode may have an important effect on the formation of the electrochemical CV peaks.

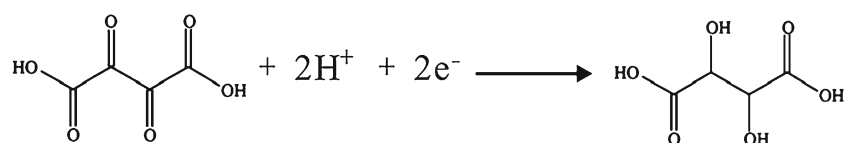
It is very interesting that two pairs of electrochemical peaks are observed at the CuGeO₃ nanowire modified glassy carbon electrode. The result is similar to that of the electrochemical behavior of cysteine at the CuGeO₃ nanowire modified electrode [12]. Therefore, the electrochemical reaction of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode is a semireversible process. In order to analyze whether the anodic and cathodic peaks are semireversible process, the experiments of initial potential scan direction and different reversal potential were carried out. It is found that the intensities of the electrochemical CV peaks maintain the same when changing the initial potential scan direction. When the potential scan reverses at different positive potential, the intensities of the electrochemical CV peaks maintain similarly. Therefore, the electrochemical CV peaks, cvp1 and cvp2, are the oxidation process of the products originated from the potential of cvp1' and cvp2', respectively. Similar to the electrochemical response of cysteine at the CuGeO₃ nanowire modified glassy carbon electrode [12], CuGeO₃ nanowires may participate in the reduction of tartaric acid, showing that it is possible for the reduction of tartaric acid to tartrate at the CuGeO₃ nanowire modified glassy carbon electrode. Fulcrand et al. [14] showed that tartaric acid can be reduced to tartrate. Therefore, cvp1-cvp1' can be assigned to the oxidation–reduction process between tartaric acid and tartrate. The reaction process for cvp1 and cvp1' may be as follows:

The oxidation process of tartaric acid is shown in Scheme 1.

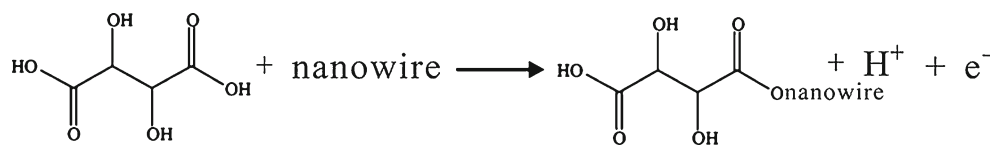
The reduction process of tartrate is shown in Scheme 2.

The electrochemical responses of different acids, such as cysteine and ascorbic acid, at different electrodes modified with different materials exhibit irreversible anodic oxidation process or one pair of semireversible redox peaks [15–17]. However, the electrochemical behavior of tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode shows two pairs of electrochemical CV peaks. Cvp1-cvp1' is

Scheme 2 The reduction process of tartrate at CuGeO₃ nanowire modified glassy carbon electrode



Scheme 3 The adsorption of tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode



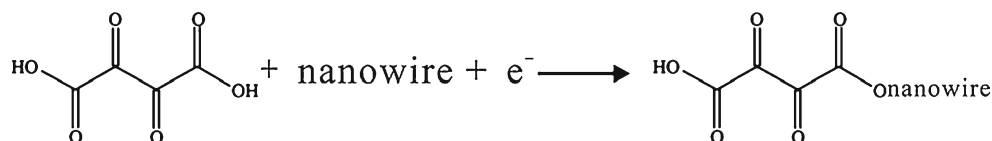
considered to be the oxidation–reduction process between tartaric acid and tartrate. However, the formation process of cvp2–cvp2' is still confusing. The adsorption–desorption behavior of cysteine has been researched by impedance spectroscopy showing the adsorption and desorption behavior of cysteine and cystine at the surface of gold electrode, respectively [18]. The electrochemical behavior of cysteine at the CuGeO₃ nanowire modified glassy carbon electrode also shows the adsorption and desorption process of cysteine at -0.04 and -0.35 V [12]. So the cvp2–cvp2' can be contributed to the adsorption and desorption process of tartaric acid and tartrate at the CuGeO₃ nanowire modified electrode.

The adsorption of tartaric acid at the CuGeO₃ nanowire modified electrode is accompanied by anodic current (cvp2, Scheme 3).

Tartrate adsorption is accompanied by cathodic current (cvp2', Scheme 4).

Scan rate plays an important role on the electrochemical behavior of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode. Figure 3a shows the CV curve of tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode in the mixed solution of 0.1 M KCl and 2 mM tartaric acid. With the decrease of the scan rate from 50 to 25 mV s⁻¹, the intensity of the CV peaks decreases obviously. Furthermore, with the scan rate increasing from 50 to 200 mV s⁻¹, the intensity of the CV peaks increases obviously. In addition, the potential of the anodic and cathodic peaks of the tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode shifts negatively with the increase of the scan rate which is similar to that reported by Li et al. [19]. The role of the scan rate on the oxidation current of the tartaric acid is also analyzed which is shown in Fig. 3b. There is a nearly linear relation between the anodic current and scan rate in the range of 25–200 mV s⁻¹ which is consistent with that reported by Li et al. [17] and Xia et al. [16]. The results show that the scan rate affects the intensity and position of the electrochemical CV peaks.

Scheme 4 The adsorption of tartrate at CuGeO₃ nanowire modified glassy carbon electrode



Effect of the concentration of tartaric acid

The detection range and detection limit of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode are determined by measuring the CV curves of the tartaric acid with various concentrations in the range of 0.01–5 mM which is shown in Fig. 4. Figure 5 is the calibration plots of the intensities of anodic peaks with the concentration of the tartaric acid. The intensity of the CV peaks of the tartaric acid at the CuGeO₃ nanowire modified electrode increases with the increase of the concentration of the tartaric acid. The linear calibration, detection limit, and correlation coefficient of the tartaric acid are analyzed in the range of 0.01–5 mM (Table 1). The correlation coefficient is 0.997 and 0.996 for cvp1 and cvp2, respectively. The detection limit is 8.9 and 7.7 μM for cvp1 and cvp2, respectively, at a signal-to-noise ratio of 3. Compared with the electrochemical behavior of the tartaric acid using other electrodes, the CuGeO₃ nanowire modified electrode exhibits a comparable linear range and detection limit [8, 20].

Effect of the electrolytes

Electrochemical response of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode has been investigated under various electrolytes with different pH values, such as KBr and Na₂HPO₄–NaH₂PO₄ (pbs), NaOH (pH=12), and H₂SO₄ (pH=2). In neutral solution, such as KBr and pbs, the electrochemical response of the tartaric acid (Fig. 6) is similar as that in KCl solution. However, the intensities of the CV peaks of tartaric acid in KBr and pbs solution decrease slightly. In addition, the potential of the CV peaks shifts to more negative direction exhibiting the better electrocatalytic performance.

Compared to the electrochemical response of the tartaric acid in neutral solution, the CV peaks of the tartaric acid are suppressed greatly in the alkaline and acidic condition (Fig. 7). Only one extremely weak CV peak is observed at

the CuGeO₃ nanowire modified glassy carbon electrode in NaOH solution, showing that the electrochemical behavior of the tartaric acid in NaOH solution is very poor. The CV curve of the tartaric acid at CuGeO₃ nanowire modified glassy carbon electrode in H₂SO₄ solution with the pH=2 demonstrates that only one CV peak is observed and the intensity of the CV peak decreases obviously. Tartaric acid is considered to react with NaOH to form sodium tartaric in alkaline solution. Hydrogen ions in the solution with low pH value inhibit the electrochemical reaction of tartaric acid to tartrate. Therefore, it is considered that the electrochemical reaction process from tartaric acid to tartrate is inhibited in

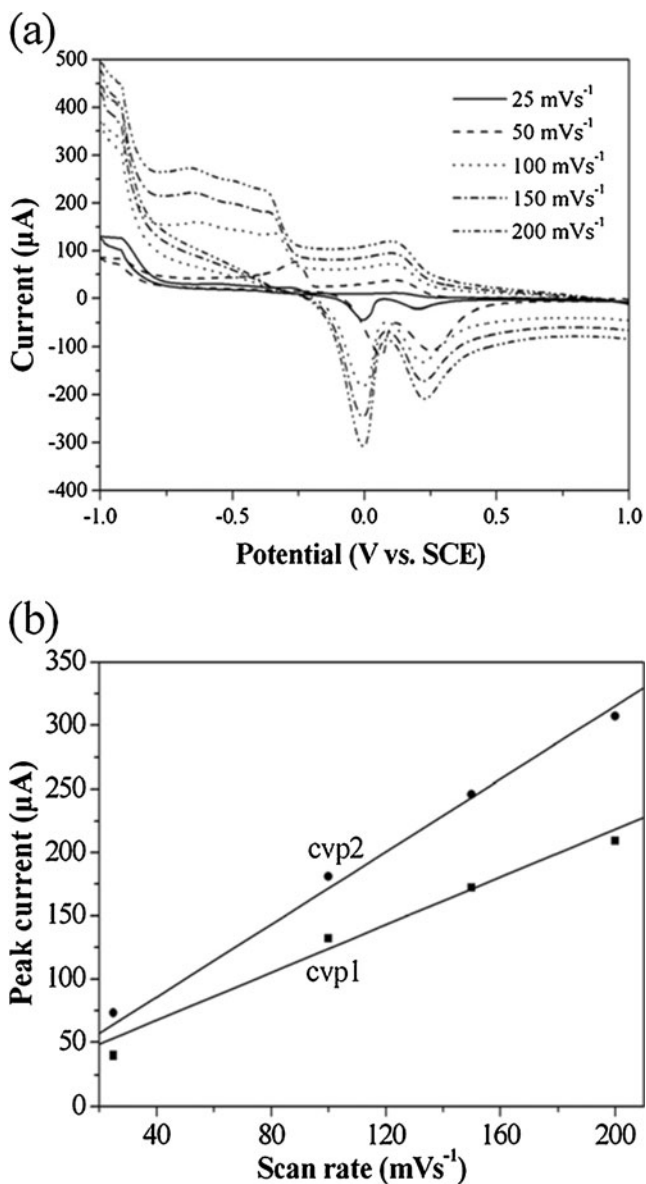


Fig. 3 a CVs of the CuGeO₃ nanowire modified glassy carbon electrode in the mixed solution of 0.1 M KCl and 2 mM tartaric acid using different scan rate. b The calibration plots of the intensities of anodic peaks against the scan rate

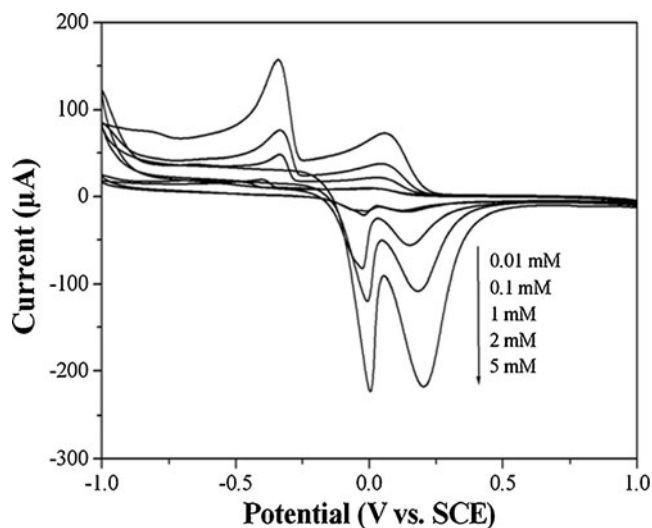


Fig. 4 CVs of the tartaric acid with different concentration at the CuGeO₃ nanowire modified glassy carbon electrode. KCl, 0.1 M, scan rate 50 mV s⁻¹

alkaline and acidic solution resulting in the decrease of intensity of the CV peaks for detecting tartaric acid.

Stability and reproducibility of the modified electrode

The stability and reproducibility of the CuGeO₃ nanowire modified electrode are analyzed in a continuous operation mode. When the same CuGeO₃ nanowire modified glassy carbon electrode repeats detection tartaric acid for the first time and 20th time in the mixed solution of 2 mM tartaric acid and 0.1 M KCl solution (Fig. 8), the RSD is 1.68% and 2.67% for cvp1 and cvp2, respectively. The CuGeO₃ nanowires are adsorbed firmly on the glassy carbon electrode. So

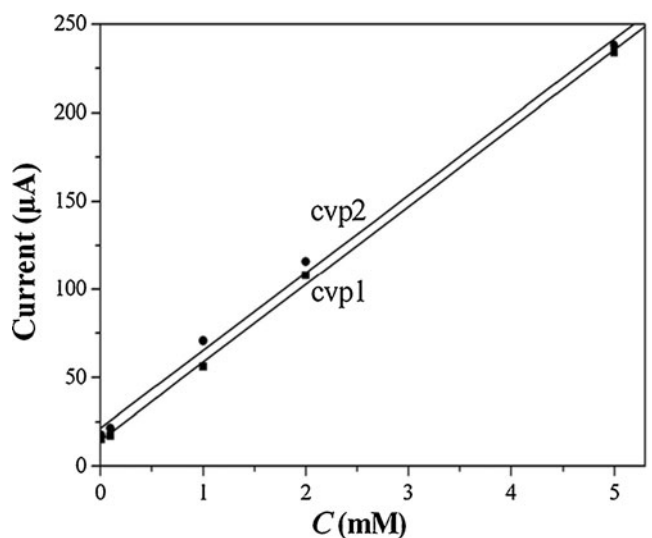


Fig. 5 The calibration plots of the intensities of anodic peaks against the concentration of the tartaric acid

Table 1 Analytical data of the tartaric acid

Electrodes and methods	CV peaks	Regression equation ^a	Correlation coefficient (<i>R</i>)	Linear range (mM)	Detection limit (μM) ^b	Reference
CuGeO ₃ nanowire modified glassy carbon electrode, electrochemical detection	cvp1	$I_p = 10.895 + 45.225C$	0.997	0.01–5	8.9	Present work
	cvp2	$I_p = 19.56 + 44.22C$	0.996	0.01–5	7.7	
Carbon, carbon-13 NMR spectroscopy					300	[8]
Disk-shaped copper electrode, electrochemical detection				0.01–0.5	0.71	[20]

^a Where I_p and C represent the peak current (in microamperes) and the concentration of the tartaric acid (in millimolars)

^b The detection limits of the tartaric acid were analyzed using a signal-to-noise ratio of 3 ($S/N=3$)

the stability of the modified glassy carbon electrode is good which is considered to be attributed to its structure stability. The time serials on the intensities of the electrochemical anodic peaks of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode are analyzed. The plots of the intensities of anodic peaks against the times (1 to 14 days) for detecting tartaric acid using the CuGeO₃ nanowire modified glassy carbon electrode are shown in Fig. 9. The results show that the CuGeO₃ nanowire modified glassy carbon

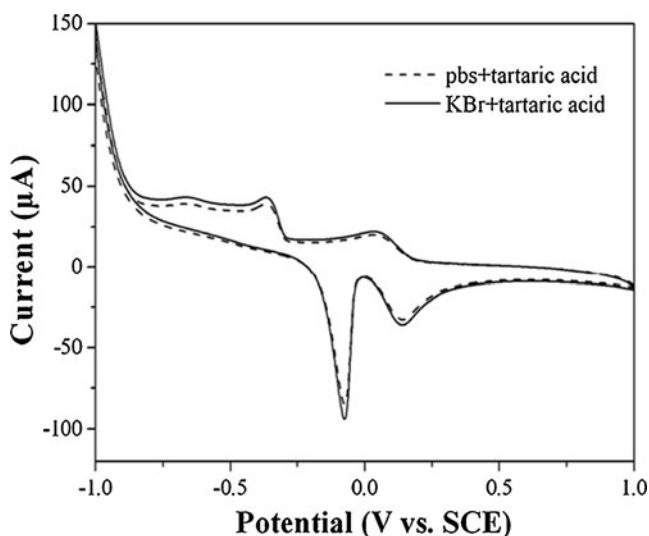


Fig. 6 CVs of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode in 0.1 M KBr and 0.1 M pbs, respectively. Tartaric acid, 2 mM, scan rate 50 mV s^{-1}

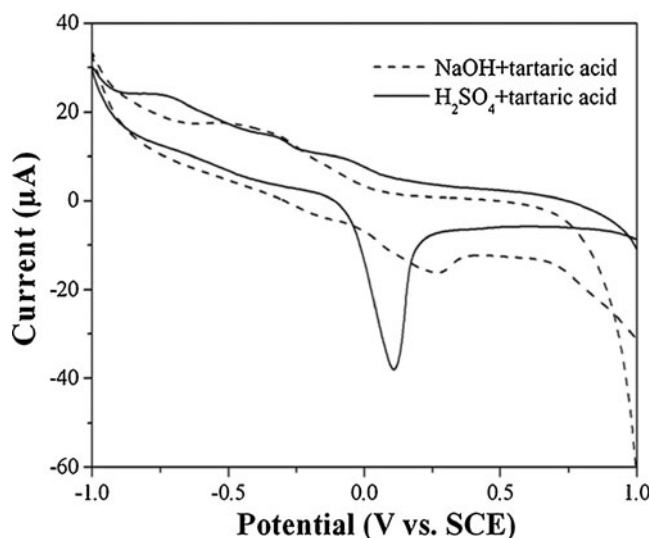


Fig. 7 CVs of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode in the NaOH and H₂SO₄ solution, respectively. Tartaric acid, 2 mM, KCl, 0.1 M, scan rate 50 mV s^{-1}

electrode can be used at least 2 weeks with only a decline in the electrochemical signal.

Conclusions

In summary, the electrochemical response of tartaric acid at the CuGeO₃ nanowire modified glassy carbon electrode shows that two pairs of semireversible electrochemical peaks are observed. The detection limit is 8.9 and 7.7 μM for cvp1 and cvp2, respectively at a signal-to-noise ratio of 3. The electrochemical behavior of tartaric acid is poor in

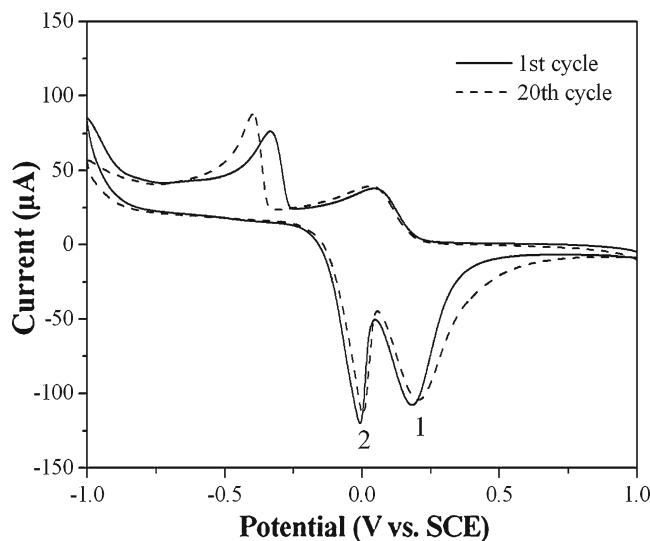


Fig. 8 CVs of the CuGeO₃ nanowire modified glassy carbon electrode in the mixed solution of 0.1 M KCl and 2 mM tartaric acid recycling for first time and 20th time, respectively. Scan rate 50 mV s^{-1}

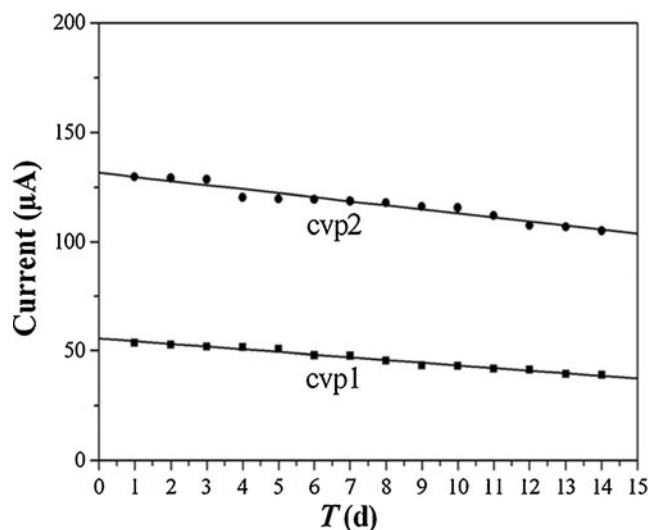


Fig. 9 The plots of the intensities of anodic peaks against the time for detecting tartaric acid using the CuGeO_3 nanowire modified glassy carbon electrode. Tartaric acid, 2 mM, scan rate 50 mV s^{-1}

alkaline solution, and the intensities of the electrochemical CV peaks decrease obviously in acidic solution. The CuGeO_3 nanowires exhibit the promising potential as the basic unit of the electrochemical sensors for detecting tartaric acid or other biological molecules.

Acknowledgments This work was supported by the Natural Science Foundation of the Education Bureau of Anhui Province of China (KJ2011A042).

References

1. Kvaratskhelia RK, Kvaratskhelia ER (2008) *Rus J Electrochem* 44:230–233
2. Yan HJ, Wang D, Han MJ, Wan LJ, Bai CL (2004) *Langmuir* 20:7360–7364
3. Palaniappan S (2001) *Eur Poly J* 37:975–981
4. Yogeswaran U, Chen SM (2008) *Sensors* 8:290–313
5. Lu Y, Yang M, Qu F (2007) *Bioelectrochemistry* 71:211–216
6. Arrieta AA, Apetrei C, Rodríguez-Méndez ML, Saja JA (2004) *Electrochim Acta* 49:4543–4551
7. Makhotkina O, Kilmartin PA (2009) *J Electroanal Chem* 633:165–174
8. Galkwad A, Silva M, Bendito DP (1994) *Analyst* 119:1819–1824
9. Liu Z, Searson PC (2006) *J Phys Chem B* 110:4318–4322
10. Ramgir NS, Zajac A, Sekhar PK, Lee L, Zhukov TA, Bhansali S (2007) *J Phys Chem C* 111:13981–13987
11. Zhang XL, Wang JX, Wang Z, Wang SC (2005) *Sensors* 5:580–593
12. Dong YP, Pei LZ, Chu XF, Zhang WB, Zhang QF (2010) *Electrochim Acta* 55:5135–5141
13. Pei LZ, Zhao HS, Tan W, Yu HY, Chen YW, Zhang QF (2009) *CrystEngComm* 11:1696–1701
14. Fulcrand H, Cheynier V, Oszmianski J, Mourounet M (1997) *Phytochemistry* 46:223–227
15. Deng CY, Chen JH, Chen XL, Wang MD, Xie Z, Yao SZ (2009) *Electrochim Acta* 54:3298–3302
16. Xia C, Ning W (2011) *Analyst* 136:288–292
17. Zhang J, Deng PH, Feng YL, Kuang YF, Yang JJ (2004) *Microchim Acta* 147:279–282
18. Hager G, Brolo AG (2009) *J Electroanal Chem* 625:109–116
19. Li Y, Zhang SH (2008) *J Disp Sci Technol* 29:1421–1425
20. Fu CG, Song LN, Fang YZ (1998) *Anal Chim Acta* 371:81–87