Highly enhanced electrocatalytic oxidation of glucose and shikimic acid at a disposable electrically heated oxide covered copper electrode

Hang Wei, Jian-Jun Sun, Liang Guo, Xiao Li and Guo-Nan Chen**

Key Laboratory of Analysis and Detection for Food Safety, Ministry of Education, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350108, P. R. China

Experimental section

Reagents. Shikimic acid was obtained from Chengdu Mansite Pharmacetical Co., Ltd., China and used as received. All the other compounds from Sinopharm chemical Reagent Co. Ltd. were at least of analytical reagent grade without any further purification. The stock solution of SA with a concentration of 1.0×10^{-2} mol L^{-1} was prepared with doubly distilled water and stored in the refrigerator at 4 °C. All the water used was purified in an ultrapure water polishing system (Research Scientific Instruments Co., Ltd., China)

Apparatus. The heating apparatus and the monitoring of the current are same as described by Sun's group.[S1] The electrochemical measurements were performed with an electrochemical analyzer (CHI440, Chenhua, China). An electrochemical cell with conventional three-electrode system was employed, a HOCE acted as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Ultraviolet-Visible Spectra for SA and its oxidation products were obtained with a Lambda 800 UV/VIS spectrometer of PerkinElmer instruments. Liquid

---

[*] Corresponding author. Tel/Fax: +86 591 22866136. E-mail: jjsun@fzu.edu.cn; gnchen@fzu.edu.cn.

chromatography/mass spectrometry experiments utilized an Agilent 1100 series LC system (Agilent Technologies, Palo Alto, CA, USA) coupled on-line to LC/MSD Trap XCT ion-trap mass spectrometer (Agilent Technologies, CA, USA) with a Zorbax C_{18} column and 1100 UV-Vis diode array detector. The mass spectrometer was equipped with an ESI source and operated in negative polarity.

Fabrication of HOCE. The diameter of copper wire used to fabricate the HOCE is 23 μm (3UEW, FUJI TECH, Japan). The layer of polyester enamel on copper wire was divested by electrically heating in atmospheric air and then wiped with diluted HCl to clean the residues of the coating. After soaking in ethanol for 3 min and rinsing with deionized water, the obtained Cu-wire was soldered onto to the prepared PCB with symmetrical construction as designed earlier by our group.[S1] The copper foil and solders were isolated by epoxy resin. Before electrochemical detection, the copper electrodes were firstly scanned in 0.1 M NaOH solution from 0.0 V to 0.8 V for several cycles until a steady-state copper oxide layer was formed.[S2]

Electrolysis Procedures. Bulk electrolysis with coulometry was performed under constant potential (0.70 V) at room temperature in a 15 mL 0.1 M NaOH solution containing 1 mM SA by using a 1 m length (∅ 0.5 mm) coiled copper wire as the working electrode.[S3] The copper anode and the platinum mesh cathode were usually maintained in two separate compartments connected by U-type agar salt bridges. The electrolyte was through with nitrogen before and during electrolysis to purge out oxygen. During electrolysis, the anode compartment was stirred continuously from below with a magnetic stirrer. The electric charge measured electrolyzing blank solution for the same time was subtracted from the total charges passed through the cell.

Results and Discussion

Calibration of the Electrode Temperature.

Calibration of the electrode temperature is quite important for the interpretation of electrochemical signals acquired with hot electrodes. Estimated by 'resistance method',[S4] the electrode temperature above the water boiling point can be reached up to ca. 150 ºC. A nearly linear relationship between temperature rise and the square of heating current was achieved at the copper wire, holding a good agreement between the experimental and the calculated values from the equations described in our earlier paper.[S1]"

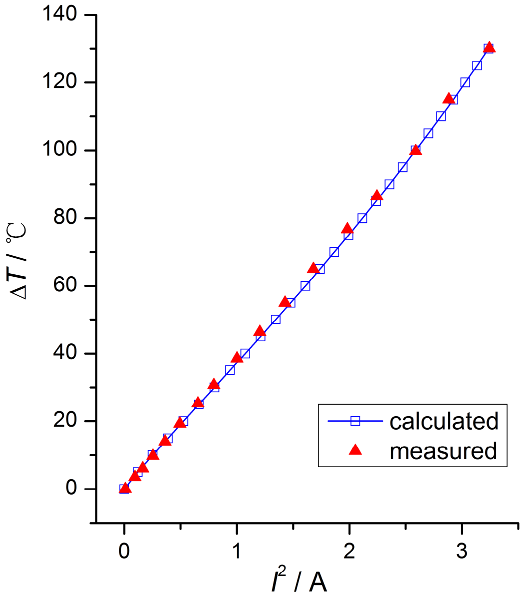

Fig. S1. Dependence of the temperature rise (ΔT) of the Cu wire on the square of heating current (I^2) in pure water. (▲measured values; —□— calculated values). Solution temperature: 20 °C.

Mechanism of Electrocatalytic Oxidation of SA at Copper Electrode

The electrocatalytic oxidation process of polyhydroxy compounds at copper electrode is generally considered to undergo several steps, including the formation of $Cu(OH)_2/CuO$ multilayer [S5]

$$Cu + 2OH^- \rightleftharpoons CuO + H_2O + 2e^- \quad \text{or} \quad Cu(OH)_2 + 2e^- \tag{1}$$

and the conversion of $Cu(OH)_2$ to CuO

$$Cu(OH)_2 \overset{\triangle}{\rightleftharpoons} CuO + H_2O \tag{2}$$

The reaction (2) is temperature sensitive and can be promoted at HOCE with elevated temperature. CuO is electrochemically oxidized to strong oxidizing agent Cu(III) species as $CuOOH^{\bullet}$ or $Cu(OH)_4^-$

$$CuO + OH^- \rightleftharpoons CuOOH^{\bullet} + e^- \quad \text{or} \quad CuO + H_2O + 2OH^- \rightleftharpoons Cu(OH)_4^- + e^- \tag{3}$$

For glucose, it is catalytically oxidated with Cu(III) and lead to C−C bond cleavage in alkaline solutions to produce lower- molecular-weight products (e.g. formate ion).[S3, S6]

$$Cu(III) + R_1{-}CHOH{-}R_2 \rightleftharpoons R_1{-}\dot{C}HO{-}R_2 + Cu(II) \tag{4}$$

Analytical Application.

Table 1. The results of regression analysis by our methods and comparison with others.

Methods	Detection temp. (°C)	Linearity (μmol L^{-1})	R^2	L.O.D. (μmol L^{-1})	R.S.D (%)	Ref.
Electrochemistry HOCE	20	20 ~ 1000	0.9975	5.0	4.1	This work
Electrochemistry HOCE	90	0.1 ~ 1000	0.9992	0.05	2.3	This work
HPLC PAD 215 nm	-	21~ 300	-	1.1	-	S7
HPLC diode array detector 213nm	25	175~ 1230	0.9995	-	1.2	S8
HPLC UV 217 nm	25	28.7~1720	0.9999	-	0.36	S9
CZE indirect UV 254 nm	-	5.74 ~ 574	0.9997	2.93	2.7	S10
HPLC UV 225nm	70	5.74 ~ 517	0.9900	1.72	7.3	S11
CZE diode array detector 213nm	18	68.9 ~ 574	0.9890	-	9.4	S11
CZE indirect diode array detector 260nm	22	5.74~ 57.4	0.9791	-	10.1	S11
MECC UV 206 nm	30	250~ 12500	0.9997	24.4	3.3	S12

References

S1 J. J. Sun, L. Guo, D. F. Zhang, W. H. Yin and G. N. Chen, *Electrochem. Commun.*, 2007, **9**, 283–288.

S2 I.-H. Yeo and D. C. Johnson, *J. Electroanal. Chem.*, 2000, **484**, 157–163.

S3 M. Z. Luo and R. P. Baldwin, *J. Electroanal. Chem.*, 1995, **387**, 87–94.

S4 P. Gründler, A. Kirbs and T. Zerihun, *Analyst*, 1996, **121**, 1805–1810.

S5 B. Miller, *J. Electrochem. Soc.*, 1969, **116**, 1675–1680; J. M. Marioli and T. Kuwana, *Electrochim. Acta*, 1992, **37**, 1187–1197; Y. Xie and C.O. Huber, *Anal. Chem.*, 1991, **63**, 1714–1719.

S6 T. R.L.C. Paixão and M. Bertotti, *J. Electroanal. Chem.*, 2004, **571**, 101–109; L. Nagy and G. Nagy, *Microchem. J.*, 2006, **84**, 70–74.

S7 T. C. Mueller, J. H. Massey, R. M. Hayes, C. L. Main and C. N. Stewart, *J. Agric. Food Chem.*, 2003, **51**, 680–684.

S8 X. Q. Wang, Y. J. Guo and C. S. Yang, *Chin. J. Chin. Mater. Med.*, 2001, **26**, 447-449.

S9 L. J. Ma and X. Liu, *J. Chin. Med. Mat.*, 2008, **31**, 63–65.

S10 C. W. Klampfl, M. U. Katzmayr and W. Buchberger, *Electrophoresis*, 1998, **19**, 2459–2464.

S11 C. Mardones, A. Hitschfeld, A. Contreras, K. Lepe, L. Gutiérrez and D. V. Baer, J. *Chromatogr. A*, 2005, **1085**, 285–292.

S12 I. L. Petersen, K. E. Andersen, J. C. Sørensen and H. Sørensen, *J. Chromatogr. A*, 2006, **1130**, 253–258.