

Electronic Supplementary Material (ESI) for RSC Advance.
This journal is © The Royal Society of Chemistry 2017

Supporting Information

Polyphenol Oxidase/Gold Nanoparticles/Mesoporous Carbon-Modified Electrode as an Electrochemical Sensing Platform for Rutin in Black Teas

Tongsheng Zhong,^{*a} Qianqiong Guo,^a Zhifang Yin,^a Xiaoyan Zhu,^a Rong Liu,^a Aijuan
Liu,^b and Shasheng Huang^a

^aHuan Provincial Key Laboratory of Dark Tea and Jin-hua, College of Materials and
Chemical Engineering, Hunan City University, Yiyang, 413000, P.R. China

^bSchool of Humanities, Beijing University of Chinese Medicine, Beijing, 100029, China

*E-mail address: tzhong67@126.com

Experimental Section

Apparatus and reagents. Pluronic F-127 ($M_w=5800$, $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$), polyphenol oxidase (PPO), and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.9%) were purchased from Sigma-Aldrich Co. Ltd. Rutin was purchased from Sinopharm Chemical Reagent Co. Ltd.. Other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd. It should be noted that phosphate buffer solution (PBS, 0.1 M) was used as the supporting electrolyte. All other chemicals and reagents were of A.R. grade and used without further purification. Prior to experiments, the solutions were purged with purified nitrogen for at least 15min to remove oxygen. Milli Q 18.2 M Ω water was used throughout the experiments.

The electrochemical experiments were carried out on CHI 760B electrochemical workstation (Chenghua Instrument Company, Shanghai, China) with a conventional three-electrode. The working electrode, the reference electrode, and the counter electrode were the modified glass carbon electrode, the saturated calomel electrode, and the Pt wire electrode, respectively. Both of cyclic voltammetry and chronoamperometry were performed in the PBS buffer solution. A small beaker with a volume of 10 mL was selected for electrochemical determination. All experiments were performed under room temperature (25 °C) except when stated otherwise. The structures of the FDU-15 mesoporous polymers were characterized by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan), transmission electron microscope (TEM, JEOL-2100, Japan) and X-ray diffractometer (XRD, SA-HF3, Rigaku Corp. Japan).

Synthesis of Mesoporous FDU-15. In a typical preparation, 3.02 g of phenol was completely dissolved in 3.0 mL of 20 wt % NaOH aqueous solution. After 10 minutes stirring, 5.3 g 37 wt % formaldehyde was added dropwise below 50 °C. Upon further stirring for 1 h at 70 °C, the mixture was cooled to room temperature. The pH value was adjusted with 0.6 M HCl solution till to ~7, and the water was removed by rotary evaporation below 45 °C, following by dissolving in anhydrous ethanol, and filtering out of NaCl to obtain the pale yellow phenolic resin precursor.

FDU-15 samples were synthesized by solvent evaporation induced self-assembly (EISA) method using copolymers F127 as a template in anhydrous ethanol. 1.0 g of F127 was dissolved in 20.0 mL anhydrous ethanol solution containing 5.0 g of phenolic resin precursor. After stirring for 30 min at 45 °C, a pale yellow homogeneous solution was obtained, and the solution was then poured into culture dish to evaporate ethanol in an oven at 45 °C for 6~8 h, followed by heating at 100 °C for 24 h. The as-made products, transparent films, were scraped from the culture dish and crushed into powders, followed by roasting under nitrogen atmosphere at 350 °C for 5 h, and dispersing in 98% sulfuric acid solution for further refluxing 24 hours to remove the template. So, the mesoporous FDU-15 was obtained through washing by ethanol and water.

Fabrication of PPO/AuNPs/ FDU-15/GCE. The GCE (3 mm in diameter) was carefully polished with 1.0-, 0.3- and 0.05- μm alumina powder successively, followed by rinsing with ultrapure water. The polished electrode was sonicated in anhydrous ethanol, $\text{HNO}_3\text{-H}_2\text{O}$ (v/v=1:1), and ultrapure water for 2~3 minutes, respectively. Then the cleaned GCE was pretreated by scanning from -0.35~1.70 V in 0.5 M H_2SO_4 at scan rate of 100 mV/s until stable signals were obtained. Finally, the electrode was rinsed with ultrapure water, and the surface of the electrode is dried with nitrogen. The as-prepared mesoporous FDU-15 (4.0 mg) was dispersed into 2 mL DMF, thus the mixture was sonicated for 1 h to form a stable suspension for standby application.

The fabrication of PPO/AuNPs/FDU-15/GCE was performed as follows: firstly, 4.0 μL of obtained stable suspension of mesoporous FDU-15 was dropped onto the pretreated GCE surface, and dried at room temperature. Secondly, Au nanoparticles were immobilized on electrode surface by cyclic voltammetry in 0.2% HAuCl_4 between 0 and 1.6 V at scan rate of 50 mV/s, then the electrode was rinsed with ultrapure water and dried at room temperature, denoted as AuNPs/FDU-15/GCE. Finally, 6 mg of polyphenol oxidase (PPO) was dissolved in 3 mL of 0.1 M PBS (pH 2.0), then the mixture was sonicated for 5 minutes. 4.0 μL of PPO solution was dropped onto the surface of the as-made AuNPs/FDU-15/GCE to obtain PPO/

AuNPs/FDU-15/GCE, which was dried in air for later use.

Anson's equation.

$$Q(t) = \frac{2nFAcD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$

where A represents the electrochemical effective surface area of the working electrode, c is the substrate concentration of potassium ferricyanide ($K_3[Fe(CN)_6]$), D is the diffusion coefficient (D is $7.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ in $K_3[Fe(CN)_6]$ solution [S1]), Q_{dl} is the charge for electric double layer (which can be eliminated by background), and Q_{ads} is the Faraday charge, and other relevant letters have their usual significance.

Table S1 Comparison of the PPO/AuNPs/FDU-15/GCE with other rutin sensors.

Electrode	Linear range (μM)	Detection limit (μM)	Ref.
poly(diallyldimethylammonium chloride) (PDDA)-functionalized graphene	0.0004–1.0	0.04 nM	12
MPA-capped Mn-doped ZnS QDs/CTAB nanohybrids	0.05-0.5 0.5-5 $\mu\text{g L}^{-1}$	0.037 $\mu\text{g L}^{-1}$	13
PABSA/GCE	0.25–10.0	0.70	S2
MWCNT/GCE	1.4–28.0, 28.0–210.0	0.71	S3
MWCNTs-GE	2.0–30.0	0.94	S4
GO–CS/GCE	0.9–90	0.56	S5
PPO/AuNPs/FDU-15/GCE	1.5-28	0.51	This work

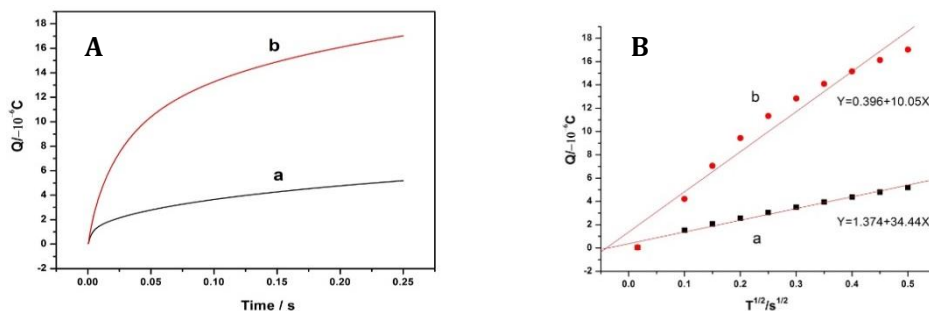


Fig. S1 Plot of $Q-t$ curves for (a) naked GCE and (b) PPO/AuNPs/FDU-15/GCE in 1.0 mM $[\text{Fe}(\text{CN})_6^{3-/4-}]$ solution containing 0.1 M KCl. (B) Linear relationship of $Q-t^{1/2}$ on (a) naked GCE and (b) PPO/AuNPs/FDU-15/GCE.

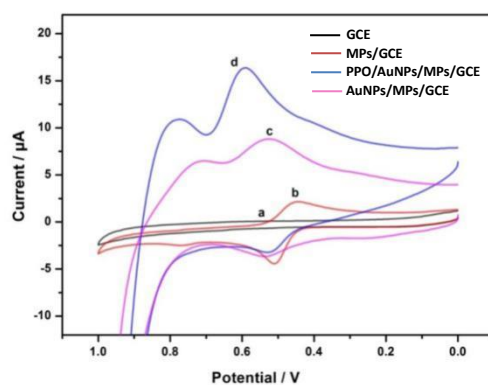


Fig. S2 CVs value of (a) GCE, (b) MPs/GCE, (c) AuNPs/MPs/GCE (d) PPO/AuNPs/MPs/GCE in PBS buffer solution (0.1 M, pH 2.0) containing 1.0 μM rutin. Scan rate, 100 mV/s.

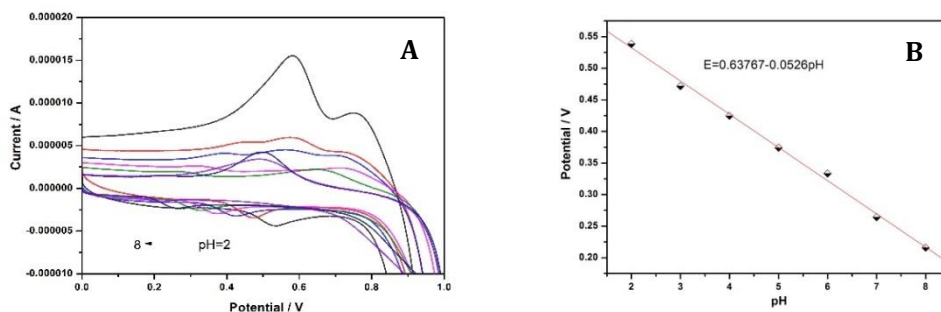


Fig. S3 (A) CVs of PPO/AuNPs/FDU-15/GCE in 0.1 M PBS containing 4.0 μM of rutin at pH value of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0. (B) Calibration curve of pH value vs the anodic peak. Scan rate, 100 mV/s.

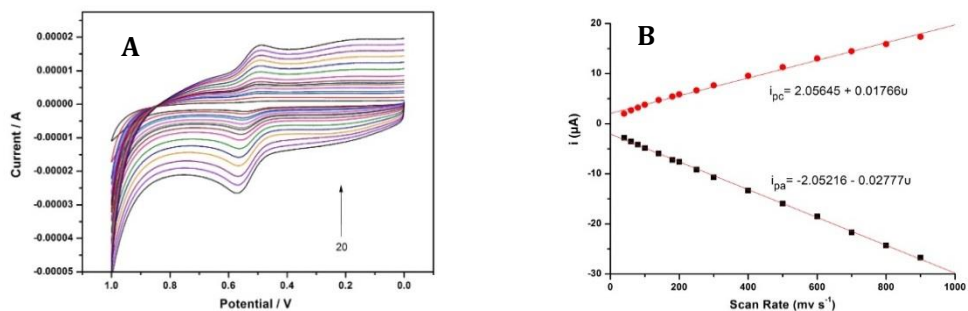


Fig. S4 (a) CV curves of 1.0 μM rutin in 0.1 M PBS buffer solution (0.1 M, pH 2.0) containing 0.1 M KCl at different scan rates: 20, 40, 80, 100, 140, 180, 200, 250, 300, 400, 500, 600, 700, 800, 900 mV s^{-1} ; (b) Calibration curve of the current vs scan rates.

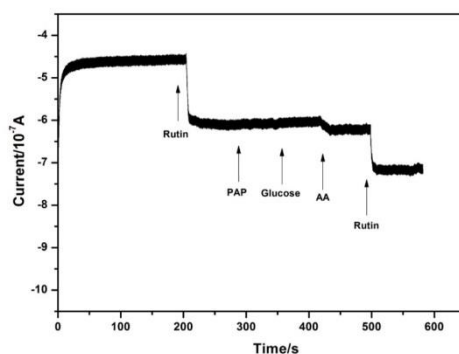


Fig. S5 Interference of different species (p-aminophenol, Glucose, Ascorbic acid) to the I-t curves for the determination of rutin.

References

- [S1] M. M. Islam, R. Kant. *Electrochim. Acta*, 2011, **56**(12), 4467-4474.
- [S2] X. Y. Chen, Z. H. Wang, F. F. Zhang, L. Y. Zhu, Y. H. Li, Y. Z. Xia. *Chem. Pharm. Bull.*, 2010, 58, 475-478.
- [S3] G. Ziyatdinova, I. Aytuganova, A. Nizamova, M. Morozov, H. Budnikov. *Collect. Czech. Chem. Commun.*, 2011, 76, 1619-1631.

[S4] L. Q. Ye, Y. Zheng, L. L. Yan, Y. T. Gao. *Adv. Mater. Res.*, 2013, 785-786, 527-532.

[S5] M. Arvand, A. Shabani, M. S. Ardaki. *Food Anal. Methods*, 2017, 10, 2332-2345.

S3 Cyclic voltammetry of natural flavonoids on MWNT-modified electrode and their determination in pharmaceuticals

Collect. Czech. Chem. Commun., 76 (2011), pp. 1619-1631

S4

S5 A new electrochemical sensing platform based on binary composite of graphene oxide–chitosan for sensitive rutin determination

Food Anal. Methods, 10 (2017), pp. 2332-2345