New Journal of Chemistry

Supporting Information

Facile construction of reduced graphene oxide-carbon dots complex embedded molecularly imprinted polymers for dual-amplifying and selective electrochemical sensing of rutoside

Huijun Guo, Rijun Gui,* Hui Jin and Zonghua Wang*

College of Chemistry and Chemical Engineering, Shandong Sino-Japanese Center for Collaborative Research of Carbon Nanomaterials, Laboratory of Fiber Materials and Modern Textile, The Growing Base for State Key Laboratory, Qingdao University, Shandong 266071, P.R. China

** E-mail: guirijun@163.com, wangzonghua@qdu.edu.cn; Tel.: +86 532 85953981*

Part S1: The preparation procedures of GO

Water-dispersible graphene oxide (GO) was prepared through the modified Hummers' method. Typically, graphite (1.0 g) was mixed with the concentrated sulfuric acid (25.0 mL) in 250 mL round-bottom flask. Then, the suspension was stirred for 24 h. After that, 1.5 g of $KMnO_4$ was slowly added into the suspension, equipped with the cooling from ice bath. The resulting mixture was stirred for additional 30 min. The temperature was increased to 60 ^{o}C and kept for 45 min. Finally, 3.0 mL of water was added twice in 15 min interval, and then 180.0 mL of water was also poured in the mixture system, so as to quench the reaction and cool down the setup.

Part S2: The preparation procedures of CDs

Carbon dots (CDs) in this work were prepared through solvothermal treatment of citric acid and urea under alkali conditions. In a typical experiment, the mixture of 1.0 g citric acid and 2.0 g urea were reacted at 160 ^{o}C for 6 h, under solvothermal conditions in 10 mL DMF. After reaction, the reaction mixture was cooled to room temperature. The obtained dark-brown solution was mixed with 20 mL aqueous solution of alkali (NaOH or KOH) (50 mg mL^{-1}), followed by stirring for 1

min and then centrifugation for 10 min at 16000 rpm. The resulting precipitates were collected, dissolved in water and centrifuged (16000 rpm, 10 min) twice to wash off residual salts and alkali, and then freeze-dried to generate dark products of CDs.

Table S1

Comparison of different electrochemical sensors for the detection of rutoside

Sensing materials	Detection ranges	LOD	Ref.
Cu-CS/MWCNT/GCE	0.5 ~100 μM	0.01 μM	[1]
RGO-MWNTs/GCE	0.6 ~1.0 mM	0.04 μM	[2]
RGO/GCE	0.1~2.0 μM	23.2 nM	[3]
NG/CILE	7.0×10^{-10}~1.0×10^{-5} M	0.23 nM	[4]
PEDOT-MeOH/GO/GCE	20 nM~10 μM	6 nM	[5]
GS/GCE	10 nM~1.25 μM	3.2 nM	[6]
β-CD@CRG/Nafion-GCE	6.0×10^{-9}~1.0×10^{-5} M	2.0×10^{-9} M	[7]
Fc-SAc/AuNPs/GCE	0.05~30 mM	1×10^{-8} M	[8]
MWNTs/DDMIMPF6	0.03~1.5 μM	0.01 μM	[9]
PDDA-Gr/GCE	0.0004~1.0 μM	0.04 nm	[10]
Gr-IL-Chit SPE	0.00106~350 mIU/mL	0.00035	[11]
Nafion-GO/CILE	0.08~80.0 μM	mIU/mL	[12]
MWCNTs/ARGO	0.01~112 mM	0.02 μM	[13]
PdNPs/GO	0.005~ 6 μM	2 nM	[14]
MIPs/RGO-CDs/GCE	0.01~6.5 μM	3 nM	This work

Abbreviations: chitosan (CS); multiwalled carbon nanotube (MWCNT); glassy carbon electrode (GCE); reduced graphene oxide (RGO); nitrogen-doped graphene (NG); carbon ionic liquid electrode (CILE); poly(hydroxymethylated-3,4-ethylenedioxythiophene) (PEDOT-MeOH); graphene oxide (GO); graphene nanosheets (GS); chemically reduced graphene (CRG); *β*-cyclodextrin (*β*-CD); ferrocene benzyne derivative (Fc-SAc); gold nanoparticles (AuNPs); 1-dodecyl-3-methylimidazolium exafluorophosphate (DDMIMPF6); poly(diallyldimethylammonium chloride) (PDDA); graphene (Gr); chitosan (Chit); 1-methyl-3-octyl imidazolium tetrafluoroborate ionic liquid (IL); screen-printed electrodes (SPE); aminate reduced graphene oxide (ARGO).

References

[1] M.B. Gholivand, L. Mohammadi-Behzad, H. Hosseinkhani, Application of a Cu-chitosan/multiwalled carbon nanotube film-modified electrode for the sensitive determination of rutin, Anal. Biochem. 493 (2016) 35-43.

[2] S.L. Yang, G. Li, M.F. Hu, L.G. Qu, Preparation of electrochemically reduced graphene oxide/multi-wall carbon nanotubes hybrid film modified electrode, and its application to amperometric sensing of rutin, J. Chem. Sci. 126 (2014) 1021-1029.

[3] Y. Lei, D. Du, L. Tang, C. Tan, K. Chen, G.-J. Zhang, Determination of rutin by a graphene-modified glassy carbon electrode, Anal. Lett. 48 (2015) 894-906.

[4] W. Sun, X.Z. Wang, H.H. Zhu, X.H. Sun, F. Shi, G.N. Li, Z.F. Sun, Graphene-MnO_2 nanocomposite modified carbon ionic liquid electrode for the sensitive electrochemical detection of rutin, Sens. Actuators B 178 (2013) 443-449.

[5] L.-P. Wu, L. Zhang, L.-M. Lu, X.-M. Duan, J.-K. Xu, T. Nie, Graphene oxide doped poly (hydroxymethylated-3,4-ethylenedioxythiophene): enhanced sensitivity for electrochemical determination of rutin and ascorbic acid, Chin. J. Polym. Sci. 32 (2014) 1019-1031.

[6] X. Yang, J. Long, D. Sun, Highly-sensitive electrochemical determination of rutin using NMP-exfoliated graphene nanosheets-modified electrode, Electroanalysis 28 (2016) 83-87.

[7] K.P. Liu, J.P. Wei, C.M. Wang, Sensitive detection of rutin based on β-cyclodextrin@chemically reduced graphene/Nafion composite film, Electrochim. Acta 56 (2011) 5189-5194.

[8] M.L. Liu, J.H. Deng, Q. Chen, Y. Huang, L.P. Wang, Y. Zhao, Y.Y. Zhang, H.T. Li, S.Z.Yao, Sensitive detection of rutin with novel ferrocene benzyne derivative modified electrodes, Biosens. Bioelectron. 41 (2013) 275-281.

[9] X. Wang, C. Cheng, R. Dong, J. Hao, Sensitive voltammetric determination of rutin at a carbon nanotubes-ionic liquid composite electrode, J. Solid State Electrochem. 16 (2012) 2815-2821.

[10] D. Miao, J. Li, R. Yang, J. Qu, L. Qu, P.d.B. Harrington, Supersensitive electrochemical sensor for the fast determination of rutin in pharmaceuticals and biological samples based on poly(diallyldimethylammonium chloride)-functionalized graphene, J. Electroanal. Chem. 732 (2014) 17-24.

[11] M. Roushani, A. Valipour, Using electrochemical oxidation of Rutin in modeling a novel and sensitive immunosensor based on Pt nanoparticle and graphene-ionic liquid-chitosan nanocomposite to detect human chorionic gonadotropin, Sens. Actuators B 222 (2016) 1103-1111.

[12] S. Hu, H. Zhu, S. Liu, J. Xiang, W. Sun, L. Zhang, Electrochemical detection of rutin with a carbon ionic liquid electrode modified by Nafion, graphene oxide and ionic liquid composite, Microchim. Acta, 178 (2012) 211-219.

[13] X.F. Zhu, J.K. Xu, X.M. Duan, L.M. Lu, H.K. Xing, Y.S. Gao, H. Sun,L.Q. Dong, T.T. Yang, Multi-walled carbon nanotubes-aminate reduced graphene oxide modified glassy carbon electrode as the voltammetric sensor for sensitive electrochemical determination of rutin, Int. J. Electrochem. Sci. 10 (2015) 9192-9204.

[14] J. Leng, P. Li, L. Bai, Y.Q. Peng, Y.F. Yu, L.M. Lu,Facile Synthesis of Pd Nanoparticles-graphene oxide hybrid and its application to the electrochemical determination of rutin, Int. J. Electrochem. Sci. 10 (2015) 8522-8530.