Int. J. Electrochem. Sci., 15 **(2020)** 7860 – 7867, doi: 10.20964/2020.08.68

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Simultaneous Detection of Catechol and Hydroquinone by Gold Nanorods/Poly(*L*-cysteine) Modified Electrode

Keying zhang[*], *Deshun Cheng, Lei Yang, Ziqiang Zhang, Xiaoling Li, Na zhang*[*]

Anhui Key Laboratory of Spin Electron and Nanomaterials; School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Anhui 234000, China.
[*]E-mail: zhangky1983@163.com ; szxyzn@163.com

Received: 15 April 2020 / *Accepted:* 11 June 2020 / *Published:* 10 July 2020

Herein, a poly(*L*-cysteine) modified glassy carbon electrode was prepared by electropolymerization. Gold nanorods were assembled onto the surface of the poly(*L*-cysteine) modified electrode surface via Au-S bonds. Scanning electron microscope was used to characterize gold nanorods. The final electrode was used for the detection of catechol and hydroquinone. The results showed that this modified electrode exhibited obvious electrocatalytic effect on catechol and hydroquinone. Differential pulse voltammetry was used to detect catechol and hydroquinone in 0.1 mol/L phosphate buffer solution (pH = 7.0). The detection limit was 2.6×10^{-7} mol/L and 1.2×10^{-7} mol/L, respectively. In addition, the proposed electrode had good stability and reproducibility, and could be used for detecting catechol and hydroquinone in samples.

Keywords: Modified electrode, Gold nanorods, poly(*L*-cysteine), Catechol, Hydroquinone

1. INTRODUCTION

Catechol (CC) and hydroquinone (HQ) have relatively high toxicity and are difficult to degrade in the natural environment. Excessive CC and HQ can cause skin diseases, have a great impact on hematopoietic function, and damage nerves[1,2]. Not only does it cause great harm to human health, but also has a great pollution hazard to the natural environment. Therefore, accurate and rapid detection of CC and HQ is of great significance. However,CC and HQ are two isomers with similar properties, and it is difficult for general methods to achieve simultaneous detection of two substances. Electrochemical methods are concerned by researchers due to their advantages [3-5]. However, due to the weak direct electrochemical properties of CC and HQ on the bare electrode, the redox peaks of the two substances in the mixture often overlap, and it is difficult to achieve the simultaneous determination [6]. Current

research shows that the modified electrode based on nanomaterials can achieve the simultaneous detection of CC and HQ [7, 8].

Gold nanorods have good electrical conductivity, and good biocompatibility[9-12]. In recent years, the electrochemical sensors based on gold nanorods have been reported. For example, Sun group studied the direct electrochemistry and electrocatalysis of myoglobin on a gold nanorods-decorated carbon ionic liquid modified electrode, and exhibited potential applications in actual sample detection[13]. The conductive polymer-based modified electrode has adjustable functional groups on the electrode surface, and has good uniformity and adhesion, which can provide a good platform for the assembly of nanomaterials. Fei group constructed a novel self-protection sensor based on an interesting thermo-sensitive triblock polymer PS-PNIPAm-PS, the detection limit of hydroquinone reached 490 nM [14]. At present, modified electrodes based on nanomaterials and polymers have been successfully prepared [15-20]. Zhang group fabricated biomass-based porous carbon nanofibre/polyaniline composites for supercapacitor electrode materials[21].

In this paper, a modified electrode modified with gold nanorods and poly(*L*-cysteine) was constructed. The electrochemical behaviors of CC and HQ on this modified electrode were studied, and the simultaneous detection of two substances was investigated. A new method for simultaneous detection of CC and HQ was developed.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

Chloroauric acid, L-cysteine, catechol (Alfa Aesar), hydroquinone (Beijing Yili Fine Chemical Co., Ltd.), other reagents are analytically pure. A mixed solution of NaH_2PO_4 and Na_2HPO_4 was used to prepare a 0.1 mol/L (pH 7.0) phosphate buffer solution (PBS), and the pH was adjusted with H_3PO_4 and NaOH; N_2 was deoxygenated and the experimental water was double distilled water.

CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Company); Three-electrode system for electrochemical measurement, using bare glass carbon electrode (GCE) or modified electrode as working electrode, saturated calomel electrode (SCE) as reference electrode, platinum wire electrode as the auxiliary electrode.

2.2 Preparation of gold nanorods/poly(L-cysteine) modified electrode

The bare glass carbon electrode was polished with Al_2O_3 powder suspension until it was bright, followed by ultrasonic cleaning with 1: 1 (V: V) HNO_3, ethanol and water for 1 min, and dried for use. The treated electrode was immersed in 0.1 mol/L PBS (pH 7.0) containing 1.0×10^{-5} mol/L L-cysteine and scanned continuously for 10 cycling by cyclic voltammetry in the potential range of -0.8 to 2.0 V, with a scan rate of 100 mV/s, then rinsed with distilled water, and dry for use. Gold nanorods were prepared according to the previous report [22], 10 μL of centrifuged gold nanorods solution was dropwised onto the modified electrode surface of poly(L-cysteine), and kept at 4 °C overnight, and the

prepared electrode was then rinsed with distilled water, the obtained electrode was donated as gold nanorods/poly(L-cysteine)/GCE (AuNRs/pL-cys/GCE).

3. RESULT AND DISCUSSION

3.1 The characterization of gold nanorods

Scanning electron microscope (SEM) was used to characterize the prepared gold nanorods. Figure 1 showed that the synthesized gold nanorods are uniform in size and can be uniformly and stably dispersed in the solution without agglomeration.

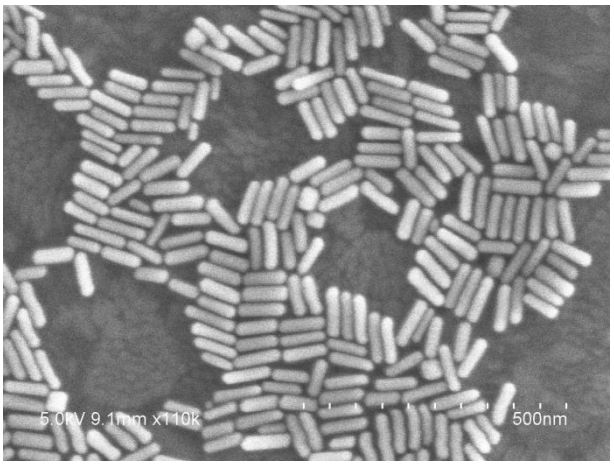

Figure 1. The SEM image of gold nanorods

3.2 Electrocatalytic CC and HQ

Figure 2 showed the CV curves of HQ (A) and CC (B) on different electrodes in 0.1mol / L PBS (pH 7.0); bare GCE (a), pL-cys/GCE (b), AuNRs/pL-cys/GCE (c). It can be seen from the figure 2, HQ and CC had a pair of weak redox peaks, which was consistent with previous reports[23,24], while a pair of obvious redox peaks was observed on AuNRs/pL-cys/GCE, and the oxidation overpotential was greatly reduced. It showed that AuNRs/pL-cys/GCE had electrocatalytic ability to the oxidation of HQ and CC. The CV responses of HQ and CC mixtures on bare GCE (a) and AuNRs/pL-cys/GCE (b) were also studied (Figure 3). On bare GCE, the redox peaks of HQ and CC were broad and overlap, and the peak potentials cannot be separated. For AuNRs/pL-cys/GCE, HQ and CC showed obvious redox peaks, the peak currents were significantly enhanced, and the oxidation peaks could be clearly separated. It means that AuNRs/pL-cys/GCE can simultaneously detect two substances.

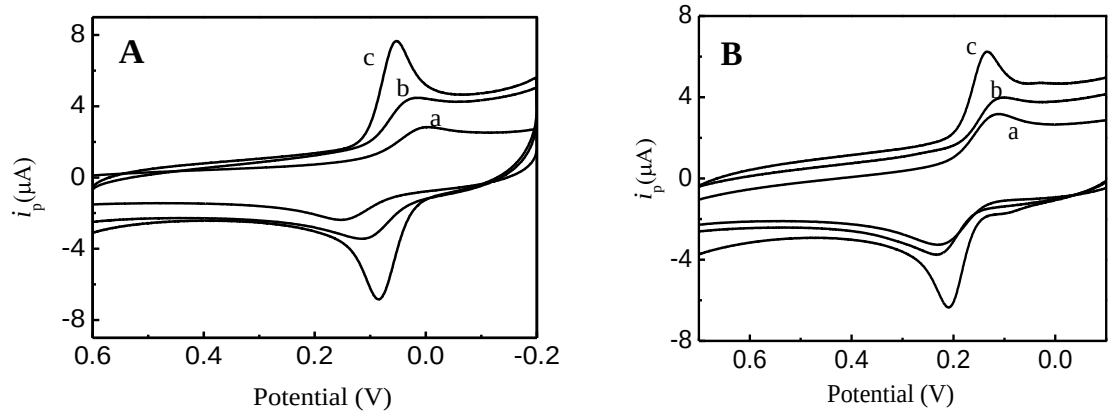

Figure 2. CVs of HQ（A）and CC (B) at the different electrodes in 0.1 mol/L PBS (pH 7.0). Scan rate: 100 mV/s. a - GCE ; b-pL-cys/GCEE; c-AuNRs/pL-cys/GCE

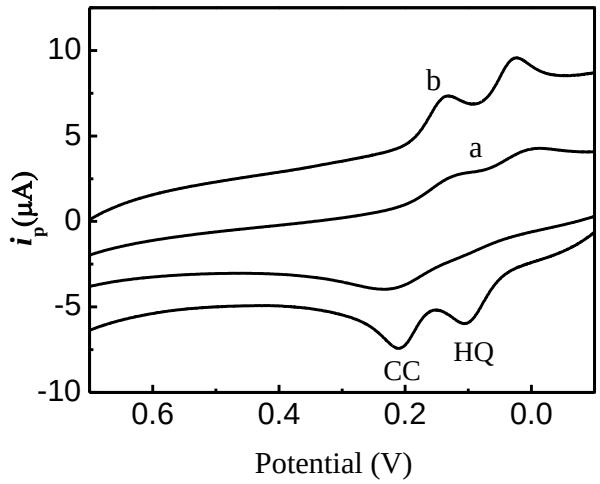

Figure 3. CVs of HQ and CC at different electrodes. Scan rate: 100 mV/s. a - GCE ; b - AuNRs/pL-cys/GCE

3.3 Effect of pH and scan rate

The influence of pH and scan rate on the electrochemical behaviors of HQ and CC was investigated by CV. The results showed that the redox peaks of CC and HQ both shift negatively with increasing pH, and their oxidation peak potential (E) has a good linear relationship with the pH , The linear equations are E (V) = 0.456-0.0466pH, R = -0.9893; E (V) = 0.6114-0.0555pH, R=-0.9928 (figure 4). The above results showed that CC and HQ had protons to participate in the reaction on the electrode surface, which were similar to previous reports[25,26]. In addition, the oxidation peak currents of HQ and CC had a linear relationship with the scan rate in the range of 20 - 200 mV/s. The linear equations were i (μA) =-1.0893- 0.01334v (mV/s) (R =-0.9943), i (μA) = -1.2694-0.0138v (mV/s) (R = 0.9887)(figure 5), respectively. indicating that the electrode reaction process of HQ and CC on the modified electrode are controlled by adsorption.

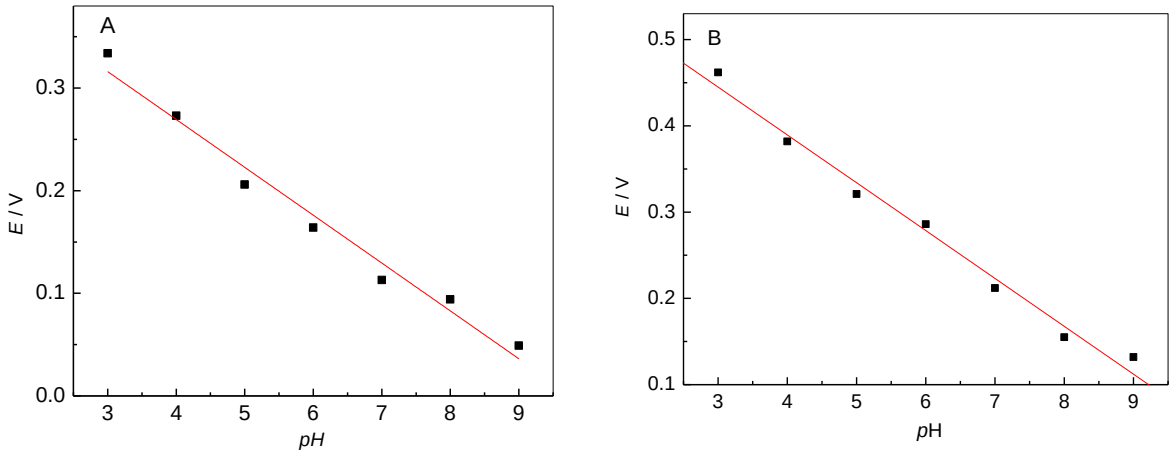

Figure 4. The effect of pH on the oxidation peak potential of HQ(A) and CC (B).

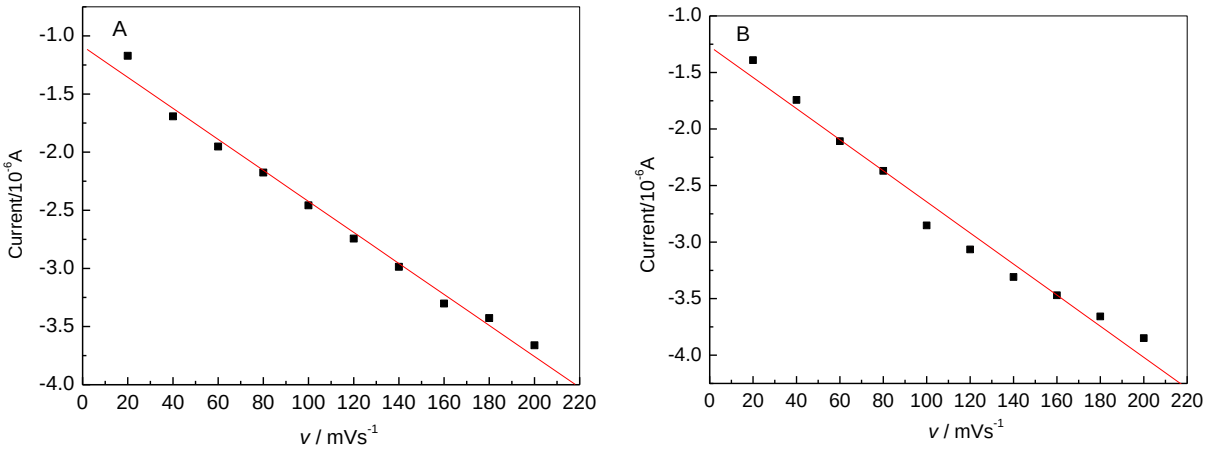

Figure 5. The effect of scan rate on the oxidation peak current of HQ (A) and CC (B).

3.4 Simultaneous determination of HQ and CC

Table 1. comparison of this paper's linear range and detection limit with published articles

Modified electrode	Linear range (HQ: 10^{-6} mol/L)	Detection limit (10^{-6} mol/L)	Linear range (CC: 10^{-6} mol/L)	Detection limit (10^{-6} mol/L)	Ref.
Poly(3,4ethylenedioxythiophene)	0.53 -860	0.42	0.52-4900	1.6	[27]
Cu-MOFGN/GCE	1.0-1000	0.59	1.0-1000	0.33	[28]
CNTs/PE	5.0-300	1.5	5.0-300	0.7	[29]
MIL-101(Cr)- rGO-CPE	10.0-1400	4.1	4.0-1000	0.66	[30]
Gold Nanorods/Poly(L-cysteine)	1.0-80	0.26	1.0-80	0.12	This work

The modified electrode can simultaneously detect HQ and CC. Figure 6 showed the DPVs of CC and HQ coexisting solution on the modified electrode. As the concentrations of CC and HQ increase, the peak current increased accordingly. And the oxidation peak currents became good linear relationship

with concentrations in the range of 1.0×10^{-6} to 8.0×10^{-5} mol/Lt, the linear equations were i (μA) =-2.9351 -0.0133c (mol/L), R = -0.9772; i (μA) = -2.5252-0.2325c (mol/L), R = -0.9881. The detection limit is 2.6×10^{-7} mol/L and 1.2×10^{-7} mol/L, respectively.The linear range and detection limit of this work were compared with previous published reports in table 1.

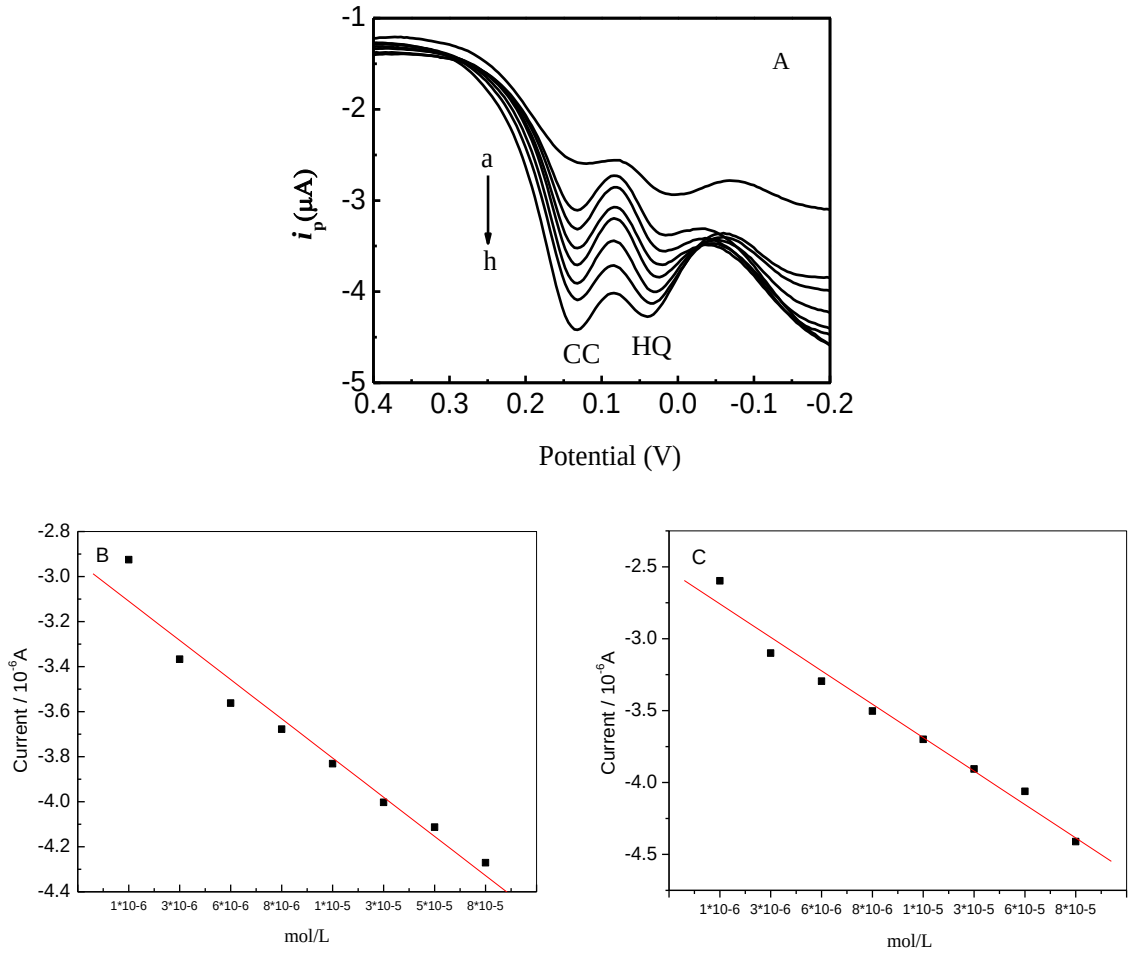

Figure 6. (A) DPVs of the different concentrations of HQ and CC in 0.1 mol/L PBS (pH 7.0) at AuNRs/pL-cys/GCE. (B) the concentration of HQ vs. oxidation peak current. (C) the concentration of CC vs. oxidation peak current

3.5 Stability and reproducibility

The prepared modified electrode was continuously scanned in 0.1 mol/L PBS (pH 7.0) for 30 cycles and placed in 0.1 mol / L pH 7.0 PBS for 3 days at room temperature, and detecting the same concentration of CC and HQ, the peak currents have no significant change, indicating that the modified electrode has good stability. The same electrode was used for the detection of HQ with the same concentration, the relative standard deviation (RSD) was 2.9%; three electrodes are prepared respectively for detecting the same concentration of HQ, RSD was 4.85%, indicating that the electrode had good reproducibility.

3.6 Interference experiment

The experiment showed that some ions at a concentration of 100 times such as K^+, Na^+, Zn^{2+}, Ca^{2+}, Fe^{3+}, Al^{3+}; 50 times the concentration of acetic acid, glacial acetic acid, ethanol; 10 times the concentration of tartaric acid, lemon Acid; the determination of CC and HQ had no obvious effect. It proved that the modified electrode had good anti-interference ability.

3.7 The real samples assay

In order to evaluate the practical application performances of the modified electrode for simultaneous detection of CC and HQ, samples of CC and HQ of different concentrations were prepared from waste water, and the recovery was measured by standard addition method with a satisfactory results (Table 2).

Table 2. Determination results of HQ and CC in the samples

No.	HQ added (10^{-6} mol/L)	Found (10^{-6} mol/L)	Recovery (%)	CC added (10^{-5} mol/L)	Found (10^{-5} mol/L)	Recovery (%)
1	4.00	3.91	97.75	4.00	3.82	95.50
2	8.00	7.86	98.25	8.00	8.14	101.75

4. CONCLUSION

In this paper, a AuNRs /pL-cys/GCE was prepared and employed to detect CC and HQ. The studies showed that the proposed electrode had excellent electrocatalytic ability on CC and HQ. And the constructed method have high sensitivity and selectivity. Additionally, the proposed electrode had good stability and reproducibility, and successfully to assay HQ and CC in samples. This research can provide a method for the detection of CC and HQ in the environmental and pharmaceutical fields.

ACKNOWLEDGEMENTS
We gratefully appreciate financial support from the Key Project of Anhui Province Excellent Talent Support Program (gxyqZD2019079); PhD Research Funding of Suzhou University (2019jb27); the Natural Science Research Key Project of Education Department of Anhui Province (KJ2017A434); the Open Research Project of Suzhou University Research Platform (2017ykf04).

References

1. L. A. Alshahrani, L. Liu, P. Sathishkumar, J. Nan, F. L. Gu, *J. Electroanal. Chem*, 815(2018)68.
2. D. L. Huang, J. Wang, F. Cheng, A. Ali, H. S. Guo, X. Ying, L. P. Si, H. Y. Liu, *Microchim. Acta,*186(2019)381.
3. O. Zitka, J. Kudr, J. Labuda, K. Xhaxhiu, V. Adam, *Electroanalysis*, 30(2018)1865.
4. S. Zhang, X. M. Zhuang, D. D. Chen, F. Luan, T. He, C. Y. Tian, L. X. Chen, *Microchim. Acta,*

186(2019)450.
5. N. Vishnu, S. Badhulika, *Biosens. Bioelectron.,* 124(2019)122.
6. A. Gutes, F. Cespedes, S. Alegret, *Biosens. Bioelectron.*, 20(2005)1668.
7. L. Zhao, J. Yu, S. Z. Yue, L. X. Zhang, Z. H. Wang, P. G. Guo, Q. Y. Liu, *J. Electroanal. Chem*, 808(2018)245
8. C. M. Kuskur, B. E. K. Swamy, H. Jayadevappa, *J. Electroanal.Chem*, 833(2019)512
9. I. Letchumanan, M. K. M. Arshad, S. R. Balakrishnan, S. C. B. Gopinath, *Biosens. Bioelectron., 130(2019)40.*
10. A. Pourjavadi, M. Bagherifard, M. Doroudianint, *Int. J. Biol. Macromol*, 149(2020)809.
11. D. Botequim, I. I. R. Silva, S. G. Serra, E. P. Melo, D.M. F. Prazeres, S.M. B. Costa, P. M. R. Paulo, *Nanoscale,* 12(2020)6334.
12. N. Li, D.C. Niu, X.B. Jia, J.P. He, Y. Jiang, J.L. Gu, Z. Li, S.A. Xu, Y.S. Li, *J. Mater. Chem. B*, 5(2017)1642.
13. C.X. Yin, W.J. Weng, R. Gao, J. Liu, Y.Y. Niu, G.J. Li, W. Sun,*J. Chin. Chem. Soc.*, 66(2019)1341.
14. P.C. Zhao, M.J. Ni, C. Chen, C.X. Wang, P.P. Yang, X.H. Wang, C.Y. Li, Y.X. Xie, J.J. Fei, *Electroanalysis*, 32(2020)1354.
15. M. Akhoundian, T. Alizadeh, M. R. Ganjali, P. Norouzi, *Talanta. 200(2019)115*
16. L. Shahhoseini, R. Mohammadi, B. Ghanbari, S. Shahrokhian, *Appl. Surf. Sci.*, 478(2019)361
17. Y. L. Tong, J. Y. Xu, H. Jiang, F. Gao, Q. Y. Lu, *Dalton T.*, 46(2017)9918.
18. X. S. Gao, Q. Q. Cai, H. K. Li, G. F. *Anal. Chem.*, 92(2020)6734.
19. J. Y. Niu, J. M. Li, P. Liu, *Langmuir*, 36(2020)4654.
20. N. Zhang, K. Y. Zhang, L. Zhang, H. Y. Wang, H. W. Shi, C. Wang, *Anal. Methods-UK*, 7(2015)3164.
21. D.B. Kong, C.Y. Qin, L. Cao, Z.M. Fang, F.L. Lai, Z.D. Lin, P. Zhang, W. Li, H.J. Lin, *Int. J. Electrochem. Sci.*, 15(2020)265.
22. X. L. Xu, Y. Y. Zhao, X. D. Xue, S. D. Huo, F. Chen, G. Z. Zou, X. J. Liang, *J. Mater. Chem. A*, 2(2014)3528.
23. Y.X. Liu, S.M. Du, J. Cao, W.S. Huang, X.R. Zhang, B.P. Qi, S.H. Zhang, B. Korean Chem. Soc., 41(2020)261.
24. N. Butwong, S. Srijaranai, J.D. Glennon, J. H. T. Luong, *Electroanalysis*, 30(2018)962.
25. Ç. C. Koçak, S. Koçak, *Electroanalysis*, 32(2019)358.
26. M. Ognjanović, D. M. Stanković, M. Fabián, A. Vukadinović, Ž. Prijović, B. Dojčinović, B. Antić, *Electroanalysis*, 30(2018)2620.
27. Y.H. Song, T. Yang, X.F. Zhou, H.T. Zheng, Shin-ichiro Suye, *Anal. Methods,* 8(2016)886.
28. J. Li, J.F. Xia, F.F. Zhang, Z.H. Wang, Q.Y. Liu, *Talanta*, 181(2018) 80.
29. A. J. S. Ahammad, T. Akter, A.A. Mamun, T. Islam, M. M. Hasan, M. A. Mamun, S. Faraezi, F. Z. Monira, J. K. Saha, *J. Electrochem. Soc*., 165 (2018)B390.
30. H.L. Wang, Q.Q. Hu, Y. Meng, Z.E. Jin, Z.L. Fang, Q.R. Fu, W.H. Gao, L. Xu, Y.B. Song, F.S. Lu, *J. Hazard Mater.,* 353(2018) 151.