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Shrimp shell-derived porous carbon and Cu-melamine metal-organic frameworks composite modified electrode for sensitive electrochemical determination of hydroquinone

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A novel electrochemical sensor based on shrimp shell-derived porous carbon (SSPC) and Cu-melamine (Cu-Me) metal-organic frameworks composite modified electrode was proposed for sensitive determination of hydroquinone (HQ). The SSPC has the enlarged active surface area, the increased conductivity, and the loading ability of Cu-Me. Attributed to these impressive features, the detection signals of HQ is greatly amplified on the SSPC/Cu-Me modified glassy carbon electrode (GCE). Under the optimized conditions, the current response of HQ on SSPC/Cu-Me/GCE is linear in the range of 5.0-1800.0 μmol/L with detection limit down to 1.83 μmol/L (3σ). The SSPC/Cu-Me/GCE exhibited excellent selectivity, stability, and reproducibility, which was utilized to detect HQ successfully in lake water sample with satisfactory recoveries. This work is expected to attract greater attention to biomass/MOF composites for electrochemical sensing.

Keywords: Shrimp shell-derived porous carbon; Cu-melamine; Composite; Hydroquinone; Electrochemical determination

1. INTRODUCTION

Hydroquinone (HQ) is widely used in different fields such as foods, pharmaceuticals, dyes, cosmetics, antioxidants, and pesticides, which is an important isomer of dihydroxybenzene in nature [1]. However, as a high toxic environmental pollutant, HQ is harmful to environment and human health [2].

Due to the easy penetration into skin and cell membrane, HQ is related to a range of diseases including liver capacity decrease, renal pipe degeneration and cancers [3]. Therefore, it is a challenge to construct an effective method for sensitive detection of HQ. At present, many methods have been applied to detect HQ, including gas chromatography-mass spectrometry, high-performance liquid chromatography, fluorescence, capillary electrophoresis, chemiluminescence, phosphorescence and electrochemical method [4-9]. Among them, electrochemical method has attracted increasing interests because of its simplicity, high sensitivity, low cost, fast response, and convenient operation [10, 11].

In recent years, carbon-based materials such as carbon nanotubes, carbon nanofibers, graphene, biomass activated carbon (AC), and their derivatives have been applied for the detection of phenolic isomers [12, 13]. Because of the abundance, large specific surface area, high porosity, low cost, and environmental friendliness, biomass materials have emerged as the most appealing precursor for porous AC [14-19]. Shrimp shell (SS) is food waste in daily life and an industrial by-product, which contains fat, protein, and chitin (polysaccharide). It has been reported as an ideal biomass candidate for converting into carbon materials by a simple pyrolysis to prepare N-doped hierarchically porous carbons (PC), which show the advantages such as different types of pores and the enhanced surface hydrophilicity [20].

Metal-organic frameworks (MOF) material is formed by the covalent/coordinate interaction between the metal ions and organic ligands. It has enormous microstructure, huge specific surface area, high porosity, tuneable pore size and plentiful metal active sites, which has great potential applications in many fields such as adsorption [21], separation [22], catalysis [23, 24], and electrochemical sensor [25-27]. Cu-melamine (Cu-Me) is formed by two-dimensional supramolecular structure via hydrogen bonds and coordination bonds, and displays block-shape nano-crystals [28, 29], which had been used in the field of catalysis.

Herein, SSPC was fabricated from waste SS by the self-templating route combined with KOH activation and subsequent $CaCO_3$ removal. The porosity of SSPC could be easily controlled by adjusting the carbonized temperature in a nitrogen atmosphere. Cu-Me was synthesized via solvothermal method to obtain block-shape crystal. The SSPC/Cu-Me composite was prepared by simple mixing SSPC and Cu-Me under ultrasonication, which was employed as the modifier for construction of electrochemical sensor to determination of HQ. With comparison to the bare glassy carbon electrode (GCE), the SSPC/Cu-Me composite modified electrode exhibited large current response, good selectivity, reproducibility, and stability.

2. EXPERIMENTAL

2.1 Materials

Shrimp (Local market of Haikou city), $CuCl_2\cdot 2H_2O$ (Guangzhou Chemical Reagent Factory), hydroquinone (HQ, Sinopharm Chemical Reagent Co., Ltd., China), melamine (Shanghai Aladdin Bio-Chem Technology Co., Ltd., China), KOH (Shanghai Aladdin Bio-Chem Technology Co., Ltd., China). Lake water sample was collected from the campus of Hainan Normal University in Guilinyang of Haikou city. The ultrapure water was filtered by an IQ-7000 instrument (Milli-Q, Germany), and all the reagents were analytically pure without further purification.

2.2 Apparatus

As-prepared materials were characterized by scanning electron microscopy (SEM, Gemini SEM 300, Germany) and transmission electron microscopy (TEM, JEOL, JEM-2100F, Japan). All electrochemical experiments were carried out by a CHI 660E electrochemical workstation (Shanghai CH Instrument, China) using a classical three-electrode system with a modified GCE (Φ=3 mm) as working electrode, a saturated calomel reference electrode (SCE) and a Pt wire auxiliary electrode.

2.3 Preparation of SSPC

As the raw material, shrimp shell (SS) was sufficiently soaked in 10 wt% HCl solution at room temperature until the completely removal of $CaCO_3$, then washed abundantly with ultrapure water and dried at 80 ℃ for 5 h. Activation process was performed with the following steps. The resultant SS and KOH were thoroughly mixed with a mass ratio of 1:1 and dried at 80 ℃ for 24 h. The dried mixture was annealed in a quartz tube under nitrogen atmosphere at carbonization temperature of 700 ℃ with a heating rate of 8 ℃/min for 1 h. Finally, the samples were thoroughly washed with ultrapure water until the solution became neutral, and the resultant SSPC was harvested by drying at 80 ℃ for 5 h.

2.4 Synthesis of Cu-Me

Cu-Me was synthesized based on the reported procedure in the literature [30]. 0.952 g of $CuCl_2 \cdot 2H_2O$, 0.711 g of melamine and 100 mL of methanol were mixed and ultrasonicated for 30 min. The solution was refluxed under magnetic stirring at 70 ℃ for 24 h and then cooled to room temperature. A block-shape crystals were obtained following washing with methanol for three times and then dried at 70 ℃ overnight.

2.5 Preparation of SSPC/Cu-Me composite modified electrode

SSPC (1.092 g) and Cu-Me (4.365 g) were added in 10 mL methanol and ultrasonicated for 30 min. Then the SSPC/Cu-Me composites were obtained after drying at 80 ℃ for 5 h. To fabricate modified electrodes, GCE was firstly polished with Al_2O_3 powders (0.03 mm), and ultrasonically cleaned in ethanol and ultrapure water. Subsequently, 8 μL of SSPC/Cu-Me suspension (2.0 mg/mL) was coated onto newly clean GCE surface and then dried under room temperature, which was denoted herein as SSPC/Cu-Me/GCE.

2.6 Electrochemical investigations

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to investigate the electrochemical properties of SSPC/Cu-Me/GCE. Phosphate buffer solution (PBS) with different pH was prepared by 0.1 mol/L Na_2HPO_4 and KH_2PO_4 solution, and used as the supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1 Materials characterizations

The morphologies of as-prepared SSPC and SSPC/Cu-Me composites were characterized by SEM. As shown in Fig. 1A, the SSPC surface exhibited abundant porous architecture, which was resulted from the KOH activation of the carbon surface that led to several interconnection nanowalls in conventional processes. From the SEM image (Fig. 1B), it could be found that the porous SSPC was blended with Cu-Me, revealing the Cu-Me block-shape crystals were successfully anchored the inner and outer walls of the pores of SSPC surface. This conclusion was further confirmed by the TEM image (Fig. 1C), in which Cu-Me block-shape crystals were well dispersed on SSPC layers. All the images proved that SSPC/Cu-Me had been successfully prepared by a simple ultrasonic mixing procedure.

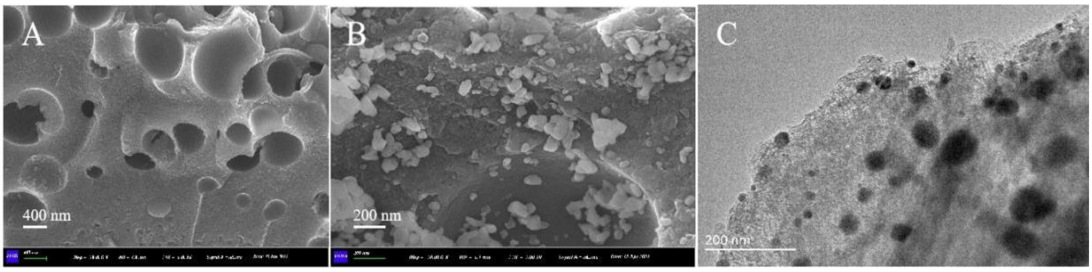

Figure 1. SEM images of (A) SSPC and (B) SSPC/Cu-Me, (C) HRTEM image of SSPC/Cu-Me.

3.2 Electrochemical behaviors of HQ

The electrochemical behaviors of HQ on bare GCE and SSPC/Cu-Me/GCE were recorded by CV. As shown in Fig. 2, there was a weak reduction peak at SSPC/Cu-Me/GCE without HQ, indicating that the reduction of the material itself might exist in SSPC/Cu-Me/GCE in the selected potential range. While in the presence of 10.0 mmol/L HQ, a pair of redox peaks can be observed and the ratio of anodic to cathodic peak currents is approximately 1.0, indicating that HQ undergoes a quasi-reversible redox reaction at SSPC/Cu-Me/GCE [31].

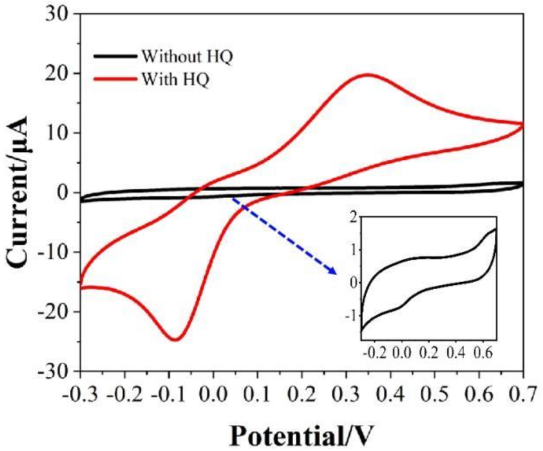

Figure 2. CV of SSPC/Cu-Me/GCE in 0.1 mol/L PBS (pH 4.0) without and with 10.0 mmol/L HQ at the scan rate of 0.1 V/s.

3.3 Effects of pH and scan rate

The influence of pH (from 3.0 to 8.0) on the CV response of SSPC/Cu-Me/GCE toward 10.0 mmol/L HQ was studied and shown in Fig. 3A. A linear regression equation between $E^{0'}$ and pH was obtained as $E^{0'}$ (mV) = -68.05 pH + 451.30 (r^2 = 0.983). The slope of the equation was close to the theoretical value of -59 $mV \cdot pH^{-1}$, indicating same amounts of electrons and protons invloved in electrode process. The maximum response current was obtained at pH 4.0, which was the best condition where enough protons were participating in the redox reaction of HQ. Therefore, pH 4.0 was chosen to detect HQ for further electrochemical studies.

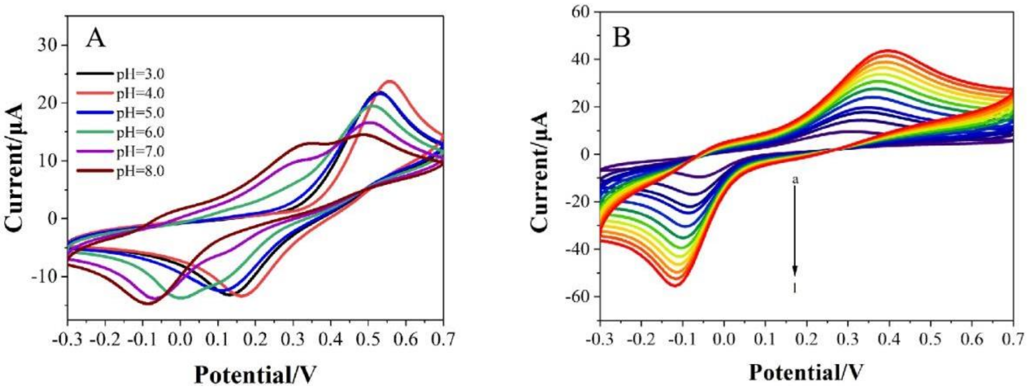

Figure 3. CV curves of SSPC/Cu-Me/GCE (A) in different pH PBS and (B) at different scan rates (a→l: 0.02, 0.05, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 V/s) in pH 4.0 PBS with 10.0 mmol/L HQ.

As depicted in Fig. 3B, the redox peak current of HQ increased with the augment of scan rate, suggesting the electrochemical behavior on the electrode is quasi-reversible. The corresponding linear regression equations can be expressed as I_{pa} (μA)=40.973 $\upsilon^{1/2}$ $(mV/s)^{1/2}$ + 8.992 (r^2=0.991) and I_{pc} (μA)= -68.328 $\upsilon^{1/2}$ $(mV/s)^{1/2}$ - 12.139 (r^2=0.986). The good linear relationships between the redox peak currents and the square root of scan rate intimated a typical diffusion-controlled process for electrocatalytic oxidation of HQ [32]. Moreover, E_p showed a linear relationship with $\ln\upsilon$ and the linear regression equations were E_{pa} (V)=0.0266 $\ln\upsilon$ (mV/s) + 0.425 (n=8, R^2=0.989) and E_{pc} (V)=-0.0256 $\ln\upsilon$ (mV/s) + 0.143 (n=8, R^2=0.994). Based on Laviron's equation, the electron transfer number (n) involved in the redox reaction of HQ was calculated to be 1.97, which was in good agreement with the previous report with two electrons involved in the HQ redox reaction [33]. The value of electron transfer coefficient (α) was further calculated as 0.51.

3.4 Calibration curve

In order to research the analytical performance of the modified electrode, DPV was applied in the following quantitative tests. Fig. 4 showed the dependence of the DPV curves on the concentrations of HQ under the optimal conditions. It was found that the oxidation peak current increased gradually with the increase of HQ concentrations, and a good linearity was observed over the range from 5.0 to

1800.0 μmol/L with the equation of I_{pa} (μA)=17.116 C (mmol/L) + 0.238 (n=14, r^2=0.995). Based on the signal-to-noise ratio (S/N) of 3, the limit of detection (LOD) was estimated to be 1.83 μmol/L. Compared with other reported modified electrodes (Table 1), the detection limit of SSPC/Cu-Me/GCE was smaller with wider linear range, which might be attributed to the synergistic effects of SSPC and Cu-Me.

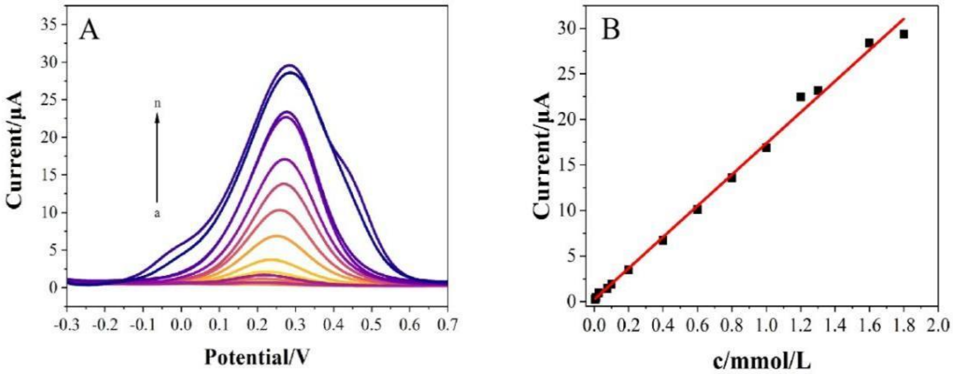

Figure 4. (A) DPV curves of different concentrations of HQ at pH 4.0 PBS by SSPC/Cu-Me/GCE (a→n: 0.005, 0.01, 0.025, 0.075, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.3, 1.6 and 1.8 mmol/L); (B) The relationship between the oxidation peak current and HQ concentration.

Table 1. Comparison of analytical parameters of HQ determination with different modified electrodes

Modified electrode	Method	Linear range (μmol/L)	LOD (μmol/L)	Reference
OV-LDHs/H-MWCNTs/GCE	DPV	0.5-150.0	0.076	[34]
Ce-MOF(TV)/CNTs/GCE	DPV	10.0-100.0	5.30	[35]
NiO/CNT/GCE	DPV	10.0-500.0	2.5	[36]
TiO_2/C900/GCE	DPV	5.0-300.0	1.24	[37]
PNR/MCPE/GCE	DPV	40.0-140.0	4.97	[38]
Co_3O_4/MWCNTs/GCE	DPV	10.0-800.0	5.6	[39]
SSPC/Cu-Me/GCE	DPV	5.0-1800.0	1.83	This work

3.5 Reproducibility, stability, and selectivity

To study the reproducibility of the sensor, six parallel prepared SSPC/Cu-Me/GCEs were used to detect 10.0 mmol/L HQ with the relative standard deviation (RSD) as 4.3 %, demonstrating the good reproducibility of SSPC/Cu-Me/GCE.

The storage stability of SSPC/Cu-Me/GCE was evaluated by storing at room temperature for two weeks, and the oxidation peak current toward 10.0 mmol/L HQ was measured every two days. After two weeks, the oxidation peak currents of the electrode remained close to its initial value, which proved that SSPC/Cu-Me/GCE had a good stability.

To check the selectivity of SSPC/Cu-Me/GCE, potential interfering substances were added to 10.0 mmol/L HQ solution (in pH 4.0 PBS). The experimental results suggested that 100 folds of inorganic ions (Fe^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- and NO_3^-) and 50 folds of glucose or hydroxyproline did not interfere to HQ detection, which confirmed that SSPC/Cu-Me/GCE possessed acceptable selectivity.

3.6 Actual sample testing

In order to evaluate the applicability of SSPC/Cu-Me/GCE, analysis of real lake water sample by the proposed method was investigated. Standard addition method was employed to calculate the recovery and the results were listed in Table 2, which were satisfactory with the recovery in the range of 97.0 % to 102.5 %. Therefore, the modified electrode could be efficiently used for the determination of HQ in water samples.

Table 2. Detection of lake water samples by SSPC/Cu-Me/GCE

Sample	Detected (μmol/L)	Added (μmol/L)	Total (μmol/L)	Recovery (%)	RSD (%)
Lake water	0.00	400.00	410.03	102.5	1.78
		600.00	609.87	101.6	1.34
		700.00	679.15	97.0	3.51

4. CONCLUSION

In summary, a novel electrochemical sensing platform was successfully developed for detection of HQ based on a composite of SSPC and Cu-Me as the sensing material. SSPC/Cu-Me composite was prepared and modified on the GCE surface, which exhibited better electroactivity towards the HQ reaction with enhanced current response. The good performance could be assigned to the large surface area of SSPC and block-shape structure of Cu-Me. The sensor displayed a lower detection limit, wider linear range, good selectivity, stability, and reproducibility under the optimized condition. Furthermore, the SSPC/Cu-Me composite modified electrode was successfully applied to detect lake water samples with satisfactory results, which extended the electrochemical applications of biomass and MOF hybridized materials.

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References

1. X.Y. Lu, S.F. Zhang, F.Y. Kong, Z.X. Wang, H.Y. Li, H.L. Fang, W. Wang, *Microchem. J.*, 166 (2021) 106246.
2. C.J. Zhang, M.M. Han, L.L. Yu, L.B. Qu, Z.H. Li, *J. Electroanal. Chem.*, 890 (2021) 115232.
3. D.A. Perry, T.M. Razer, K.M. Primm, T.Y. Chen, J.B. Shamburger, J.W. Golden, A. R. Owen, A.S. Price, R.L. Borchers, W.R. Parker, *J. Phys. Chem. C.*, 117 (2013) 8170-8179.
4. L.L. Huang, Y.Y. Cao, D.F. Diao, *Sensor. Actuat. B-Chem.*, 305 (2020) 127495.
5. A.R. Lopes da Silva, A. Jhones dos Santos, C.A. Martínez-Huitle, *RSC Adv.*, 8 (2018) 3483-3492.
6. H. Yang, S.X. Li, H.W. Yu, F.Y. Zheng, L.X. Lin, J. Chen, Y.H. Li, Y. Lin, *Nanoscale*, 11 (2019) 8950-8958.
7. U. Rajaji, M. Govindasamy, S.M. Chen, T.W. Chen, X. Liu, S. Chinnapaiyan, *Compos. Part B-Eng.*, 152 (2018) 220-230.
8. S.J. Meng, Y. Hong, Z.Y. Dai, W. Huang, X.C. Dong, *ACS Appl. Mater. Inter.*, 9 (2017) 12453-12460.
9. X.X. Liu, J. Yang, J. Cheng, Y. Xu, W. Chen, Y.C. Li, *Sensor. Actuat. B-Chem.*, 337 (2021) 129763.
10. Z. Ye, Q.W. Wang, J.T. Qiao, Y.Y. Xu, G.P. Li, *Analyst*, 144 (2019) 2120-2129.
11. N. M. Modawe, A. Edris, Y. Sulaiman, *Ecotox. Environ. Safe.*, 203 (2020) 111026.
12. L. Hu, F. Peng, D. Xia, H. He, C. He, Z. Fang, J. Yang, S. Tian, V.K. Sharma, D. Shu, *ACS Sustain. Chem. Eng.*, 6 (2018) 17391-17401.
13. N. Sivaraman, V. Duraisamy, S.M. Senthil Kumar, R. Thangamuthu, *Chemosphere*, 307 (2022) 135771.
14. F. Shi, L.J. Yan, X.Q. Li, C.L. Feng, C.Z. Wang, B.X. Zhang, W. Sun, *J. Chin. Chem. Soc.*, 68 (2021) 2006-2012.
15. Y.J. Ai, J. Liu, L.J. Yan, G.J. Li, X.H. Wang, W. Sun, *J. Chin. Chem. Soc.-Taip.*, 69 (2022) 359-365.
16. H. Cheng, J. Liu, Y.X. Sun, T. Zhou, Q.Y. Yang, S.Y. Zhang, X.P. Zhang, G.J. Li, W. Sun, *RSC Adv.*, 10 (2020) 42340-42348.
17. B.L.Wang, F. Shi, Y.X. Sun, L.J. Yan, X.P. Zhang, B. Wang, W. Sun, *Appl. Surf. Sci.*, 572 (2022) 151480.
18. J. Liu, H. Cheng, H. Xie, G.L. Luo, Y.Y. Niu, S.Y. Zhang, G.J. Li, W. Sun, *RSC Adv.*, 9 (2019) 33607-33616.
19. H. Cheng, W.J. Weng, H.Xie, J. Liu, G.L. Luo, S.M. Huang, W. Sun, G.J. Li, *Microchem. J.*, 154 (2020) 104602.
20. L. Qin, Z.P. Zhou, J.D. Dai, P. Ma, H.B. Zhao, J.S. He, A. Xie, C.X. Li, Y.S. Yan, *J. Taiwan Inst. Chem. E.*, 62 (2016) 228-238.
21. X. Zhao, Y. Wang, D.S. Li, X. Bu, P. Feng, *Adv. Mater.*, 30 (2018) 1705189.
22. H. Li, L. Li, R.B. Lin, W. Zhou, Z. Zhang, S. Xiang, B. Chen, *EnergyChem*, 1 (2019) 100006.
23. J. Long, Y. Wang, H.L. Jiang, Q. Xu, *Adv. Mater.*, 30 (2017) 1703663.
24. D. Li, H.Q. Xu, L. Jiao, H.L. Jiang, *EnergyChem*, 1 (2019) 100005.
25. G.L. Luo, R.Y. Zou, Y.Y. Niu, Y. Zhang, B.X. Zhang, J. Liu, G.J. Li, W. Sun, *J. Pharmaceut. Biomed.*, 190 (2020) 113505.
26. G.L. Luo, Y. Deng, X.P. Zhang, R.Y. Zou, W. Sun, B.H. Li, B. Sun, Y.B. Wang, G.J. Li, *New J. Chem.*, 43 (2019) 16819-16828.
27. G.L. Luo, Y. Deng, L. Zhu, J. Liu, B.X. Zhang, Y. Zhang, W. Sun, G.J. Li, *Microchim. Acta*, 187 (2020) 546.

28. J.K. Gao, J.P. Wang, X.F. Qian, Y.Y. Dong, H. Xu, R.J. Song, C.F. Yan, H.C. Zhu, Q.W. Zhong, G.D. Qian, J.M.Yao, *J. Solid State Chem.*, 228 (2015) 60-64.
29. C. Chen, C.W. Yeh, J.D. Chen, *Polyhedron*, 25 (2006) 1307-1312.
30. X. L. Zhou, J. C. Dong, Y. H. Zhu, L. M. Liu, Y. Jiao, H. Li, Y. Han, K. Davey, Q. Xu, Y. Zheng, S. Z. Qiao, *J. Am. Chem. Soc.*, 143 (2021) 6681-6690.
31. M. Yang, H. Guo, L. Sun, N. Wu , M.Y. Wang, F. Yang, T.T. Zhang, J.Y. Zhang, Z.L. Pan, W. Yang, *Colloid. Surface. A*, 625 (2021) 126917.
32. S. S. Ming, N.S.K. Gowthaman, H.N. Lim, P. Arul, E. Narayanamoorthi, I. Ibrahim, H. Jaafar, S.A. John, *J. Electroanal. Chem.*, 883 (2021) 115067.
33. S. Erogul, S. Z. Bas, M. Ozmen, S. Yildiz, *Electrochim. Acta*, 186 (2015) 302-313.
34. Z.H. Liu, D. Liao, J.G.Yu, X.Y. Jiang, *Microchem. J.*, 175 (2022) 107216.
35. H.P. Huang, Y..Chen, Z.Z. Chen, J.L. Chen, Y.M. Hu, J.J. Zhu, *J. Hazard. Mater.*, 416 (2021) 125895.
36. L. Zhao, J. Yu, S.Z. Yue, L.X. Zhang, Z.H. Wang, P.R. Guo, Q.Y. Liu, *J. Electroanal. Chem.*, 808 (2018) 245-251.
37. Z.Y. Wang, M.S. Li, Y.X. Ye, Y.S. Yang, Y.Q. Lu, X.L. Ma, Z.J. Zhang, S.C. Xiang, *J. Solid State Electr.*, 23 (2019) 81-89.
38. T.S.S.K. Naik, B.E.K. Swamy, *J. Electroanal. Chem.*, 804 (2017) 78-86.
39. Y.W. Song, M.G. Zhao, X.T. Wang, H.Y. Qu, Y. Liu, S.G. Chen, *Mater. Chem. Phys.*, 234 (2019) 217-223.