An Electrochemical Sensor Based on Co-MOF/CMK-3 for the Detection of Ofloxacin

Hao Zhang, Huiting Yang, Ruichao Wu, Ruyi Feng, Chaoliang Lei, Huixiang Yan[*]

College of Advanced Materials Engineering, Jiaxing Nanhu University, Jiaxing 314001, Zhejiang, China

Abstract: In this paper, a new green electrochemical sensor was constructed, and the Co-MOF material was synthesized by a simple one-step synthesis method. The Co-MOF/CMK-3 composite was modified on the surface of glassy carbon electrode (GCE) to construct an electrochemical sensor, and the electrochemical behaviours of the Co-MOF/CMK-3 modified electrode were investigated by CV and DPV. The developed Co-MOF/CMK-3 electrochemical sensor achieved quantitative detection of OFL. Under the optimal experimental conditions, the Co-MOF/CMK-3/GCE sensor exhibited a wide linear ranging from 1×10^{-6} to 2×10^{-5} mol/L.

1. Introduction

Ofloxacin (OFL), also known as fluazinic acid, is a third generation quinolone. It is commonly used in the treatment of respiratory, urinary, intestinal, skin, joint, and soft tissue diseases and is used by veterinarians as a growth promoter in animal therapy [1]. This class of antibiotics can often be detected in various wastewater and natural water bodies. Higher concentrations of OFL have been detected in various aquatic environments both at home and abroad [2]. 390 ng/L of OFL was detected in the surface waters of China, which is posing a serious hazard to the environment [3].

To date, a number of methods have been reported for the detection of OFL, including spectrophotometry [4], fluorescence [5], high performance liquid chromatography (HPLC) [6], capillary electrochemistry [7], and electrochemical analysis. Despite the high sensitivity and low detection limits of these methods, the instruments are usually expensive, complex and require specialised technicians to operate. Therefore, it is more convenient and faster to detect OFLs using electrochemical analysis.

MOFs have the advantages of large specific surface area, adjustable pore size, moderate pore volume, and high porosity, compared with traditional porous materials, which have crystalline structure, porous, and strong metal-ligand interaction characteristics, but their electrical conductivity is poor. Guo et al [8] constructed a sensitive electrochemical sensor for hydrazine and nitrobenzene using Co-MOF-MPC composites.The successful preparation of Co-MOF-MPC not only promotes the development of new porous composites, but also brings great hope for the design

of electrochemical sensors.

CMK-3, due to its ordered two-dimensional hexagonal structure, highly reactive porous specific surface area, good electrical conductivity, thermal stability, simple operation, and low fabrication cost, is considered as a promising material, greatly expanding its applications in the fields of chemocatalysis, physical adsorption, chemical reactions, energy storage and biosensors. Li Y. et al [9] constructed a simple sensor for bisphenol A (BPA) based on ordered mesoporous carbon CMK-3 and nanocarbon ionic liquid. CMK-3 exhibits superb electrical conductivity. Therefore, the electrochemical sensors constructed by composites prepared with MOFs and CMK-3 can combine their advantages, and the good conductivity of CMK-3 makes up for the poor conductivity of MOFs.

In this thesis, a metal-organic material (Co-MOF) composite with ordered mesoporous carbon (CMK-3) was prepared to construct an electrochemical sensor for the detection of ofloxacin. Co-MOF was prepared by one-step synthesis. The high porosity and thermal stability of MOFs materials, as well as their high surface adsorption and stability. With the stability and high electrical conductivity of the CMK-3, the Co-MOF/CMK-3 composites provides a good sensitivity, selectivity, reproducibility, and stability of the electrochemical sensor for rapid detection of ofloxacin.

2. Experimental

2.1. Synthesis of Co-MOF Materials

The synthesis of Co-MOF was mainly referred to the reported paper [10]. 10 mL of acetonitrile was stirred with 10 mL of ultrapure water for 10 min. Then, 1.4 g of cobalt nitrate was added and stirred until dissolved to obtain the mixture A. 30 mL of acetonitrile was stirred with 30 mL of ultrapure water for 5 min. And then 0.24 g of sodium hydroxide was added and stirred uniformly, and 0.48 g of pyridine 3,5 dicarboxylic acid was added into the mixture and stirred at room temperature for 12 h. The above mixture was filtered to obtain a pink precipitate and washed with ultrapure water and anhydrous ethanol several times and dried to obtain Co-MOF.

2.2. Preparation of Co-MOF/CMK-3 Composites

4 mg of Co-MOF and 4 mg of CMK-3 were dissolved in 1 mL of water and dispersed by ultrasonication for 30 min to obtain the Co-MOF/CMK-3 composite dispersion.

2.3. Configuration of Standard Solution of Ofloxacin

The OFL powder was accurately weighed and prepared into a 1.0 mmol/L OFL solution with deionised water, sealed, and stored in a refrigerator at 4 ℃. Phosphate buffer solutions (PBS) of different pH values were prepared by 0.2 mol/L Na_2HPO_4 and 0.2 mol/L NaH_2PO_4 in different ratios and modulated with 1.0 mol/L H_3PO_4. Therefore, the reagents used in the experiments were of domestic analytical purity, and all experimental procedures were carried out under the condition of room temperature.

2.4. Preparation of Modified Electrodes

The bare glassy carbon electrode was polished with Al_2O_3 polishing powder and then ultrasonically cleaned with distilled water and anhydrous ethanol for 5 min, and the electrode was blown dry with a wash ball for spare. Take 5 μL of Co-MOF/CMK-3 composite dispersion

uniformly drop-coated on the treated glassy carbon electrode, and put it under the infrared lamp for drying, which was recorded as Co-MOF/CMK-3/GCE, and the modified electrode was prepared as shown in Figure 1. The parameters of cyclic voltammetry (CV) are potential range: -0.2~0.6 V; rest time: 2 s; sweep rate: 0.1 V/s. The parameters of differential pulse voltammetry (DPV) are scanning potential range: 0.8-1.5 V; rest time: 2 s; potential increment: 0.004 V; pulse amplitude: 0.05 V; sample width: 0.0167 s; pulse period: 0.5 s.
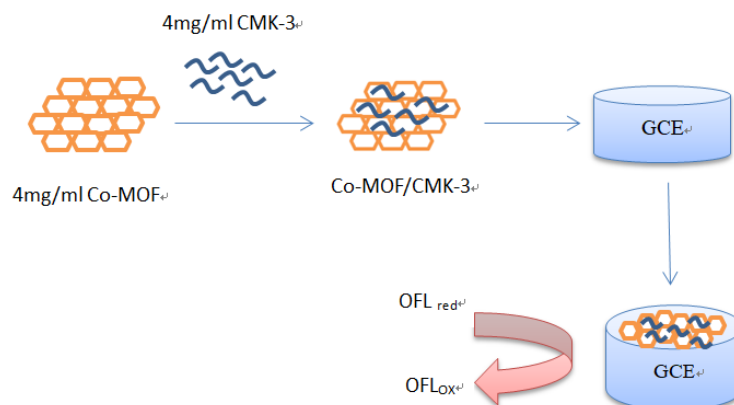

Figure 1. Schematic illustration of the electrochemical sensor based on Co-MOF/CMK-3 for OFL detection.

3. Results and Discussion

3.1. Characterisation of Different Materials

Scanning electron microscope (SEM) images of Co-MOF, CMK-3, and Co-MOF/CMK-3 are shown in Figure 2. It can be observed that the Co-MOF crystals are in the form of columns with a relatively smooth surface, and the CMK-3 is in a two-dimensional hexagonal structure, and the folded and stacked structure of the CMK-3 is clearly seen. From Figure 2 (3), it can be seen that the two materials are stacked on top of each other with a larger specific surface area, which indicates that the composite material was successfully synthesised. The microporous and mesoporous structure and large specific surface area of Co-MOF/CMK-3 provide a larger sensing area and more active sites for the application of this material in electrochemical sensing, and endowed with higher electrochemical activity [11].
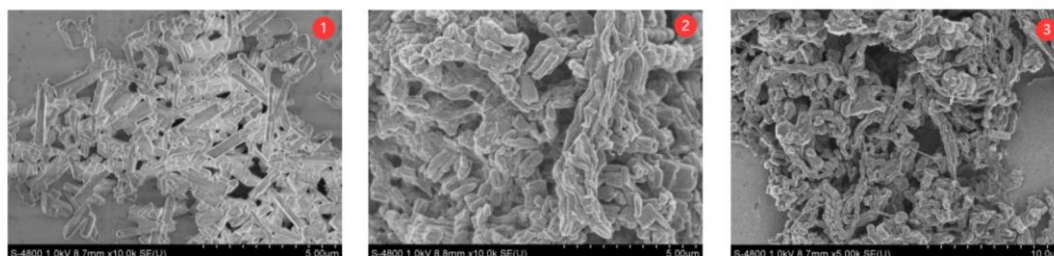

Figure 2. SEM images of (1) Co-MOF; (2)CMK-3; (3) Co-MOF/CMK-3

3.2. Electrochemical Behaviour of Differently Modified Electrodes

Potassium ferricyanide ($K_3[Fe(CN)_6]$) and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were selected as electrochemical probes to investigate the electrochemical properties of various modified

electrodes by cyclic voltammetry (CV) as shown in Figure 3. The electrodes were characterised with a potential range of -0.2 to 0.6 V/s and a sweep rate of 0.1 V/s in a solution containing 5 mM $K_4[Fe(CN)_6]$ and 5 mM $K_3[Fe(CN)_6]$, respectively, with GCE and Co-MOF/CMK-3/GCE modified electrodes as working electrodes. A pair of obvious redox peaks with a peak potential difference of 0.141 V was visible on the bare electrode.When the bare electrode was modified with Co-MOF/CMK-3, the peak current was clearly higher than that of the bare electrode, and the difference of the redox peak potential ΔEp was also reduced from 0.141 V to 0.123 V, indicating that the Co-MOF/CMK-3/GCE has a good electrical conductivity and large specific surface area, which accelerated the redox process of $[Fe(CN)_6]^{3-/4-}$. The results indicate that the modification of Co-MOF and CMK-3 can improve the electrochemical activity of the electrode interface.
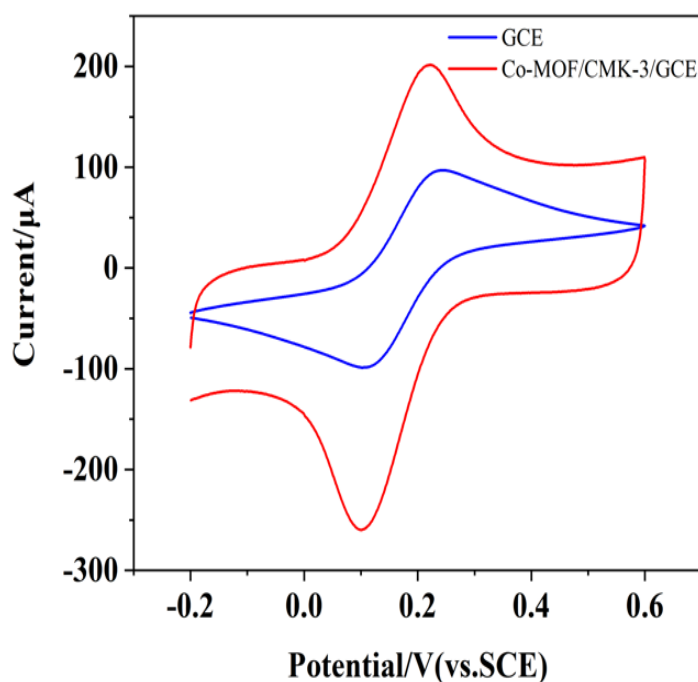

Figure 3. CVs of different modified electrodes under the mixture solution of 5 mM K4[Fe(CN)6] and 5 mM K3[Fe(CN)6])

3.3. Electrochemical Behaviour of Modified Electrodes with OFL

As shown in Figure 4, the DPV signals of OFL were measured by GCE and Co-MOF/CMK-3/GCE electrodes in a solution containing 5 μM OFL of 0.2 M PBS (pH = 7), respectively. Under the same experimental conditions, the bare glassy carbon electrode had a weak oxidation peak at a peak potential of 1.200 V with a peak current of 18.93 μA, whereas there was a significant increase in the response peak current of OFL with a peak current of 36.59 μA and a peak potential of 1.124 V when the Co-MOF/CMK-3/GCE electrode was used. The Co-MOF/CMK-3/GCE electrode resulted in a 1.94-fold increase in the peak current value of OFL compared with that of the bare glassy carbon electrode, and the peak potential was finally shifted negatively by 76 mV, suggesting that the synergistic catalytic effect of Co-MOF and CMK-3 improved the sensitivity of the OFL response at the electrode.
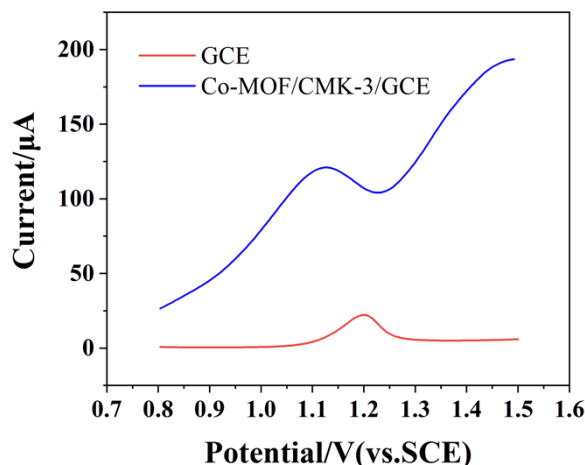
Figure 4. DPV responses of the electrochemical sensor of Co-MOF/CMK-3/GCE and GCE toward OFL

3.4. Optimisation of Experimental Conditions

In order to investigate the effect of pH on the electrochemical behaviour of Co-MOF/CMK-3/GCE, the effect of PBS with different pH values (pH=5~8) on the oxidation peak potentials and peak currents of Co-MOF/CMK-3/GCE on the oxidation peaks was investigated. As shown in Figure 5, the Co-MOF/CMK-3/GCE oxidation peak current difference gradually increased with the increase of pH between 5.0 and 7.0; the oxidation peak current difference reached a peak value of about 26.34 µA at pH 7.0; when the pH value was varied between 7.0 and 8.0, a significant decrease in the oxidation peak current difference of the OFL occurred. The peak current difference in the alkaline environment decreased faster than in the acidic environment, and the rate of decrease was asymmetric on both sides. Therefore, the optimum pH 7.0 of PBS was chosen.
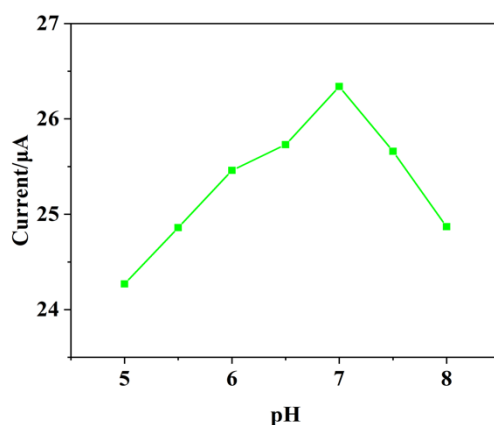

Figure 5. Optimization of different pH (pH = 5, 5.5, 6, 6.5, 7, 7.5, 8) toward OFL based on Co-MOF/CMK-3/GCE sensor

3.5. Linear Range of OFL Detection by Co-MOF/CMK-3/GCE Sensor

The DPV detection method is more sensitive than the CV detection method, this paper utilises the DPV method under optimal experimental conditions to detect the response of a series of concentrations of OFL solutions on the Co-MOF/CMK-3/GCE sensors. It can be seen in Figure 6 that as the the concentration of OFL in PBS solution increases continuously (the concentration

range is 1 μM~20 μM), the current also increases continuously, and the concentration shows a good linear relationship with the peak of the electrical signal. The linear regression equation of the peak current with the concentration of OFL at concentration values between 1 μM and 20 μM is Ip (μA) = 1.2922 C (μM) + 28.509 (R^2=0.9909).
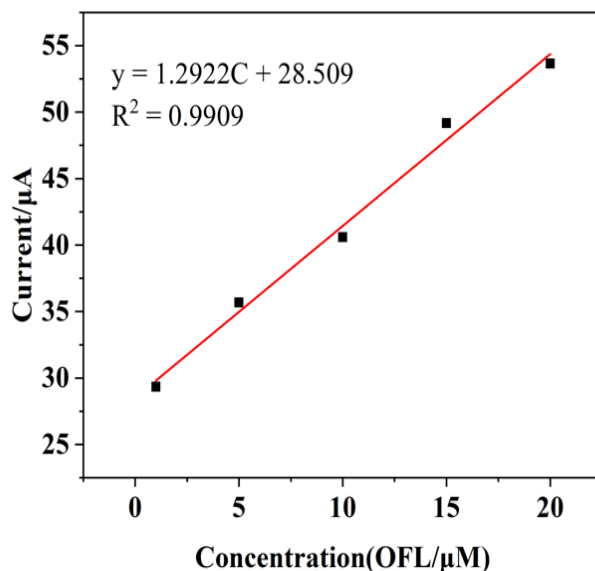

Figure 6. The calibration curve of the Co-MOF/CMK-3/GCE sensor for detecting OFL at different concentrations

4. Conclusion

In summary, an electrochemical sensor was successfully constructed for sensitive detection of ofloxacin using Co-MOF/CMK-3 composite. The synthesised materials were characterised using SEM. The electrochemical behaviour of Co-MOF/CMK-3/GCE for OFL was investigated by electrochemical analysis methods such as CV and DPV. Under the optimal experimental condition, Co-MOF/CMK-3/GCE exhibits a good electrochemical response to OFL detection with a linear regression equation of Ip (μA) = 1.2922 C (μM) + 28.509 (R^2 = 0.9909). The novel electrochemical sensor can be used as a rapid detection method for OFL.

Funding

Data Availability

The datasets used during the current study are available from the corresponding author on reasonable request.

Conflict of Interest

The author states that this article has no conflict of interest.

References

[1] Deng Y, Debognies A, Zhang Q, et al. *Effects of ofloxacin on the structure and function of freshwater microbial communities* . *Aquatic Toxicology*, 2022, 244:106084.

[2] Taherizadeh M, Jahani S, Moradalizadeh M, et al. *Synthesis of a dual-functional terbium doped copper oxide nanoflowers for high-efficiently electrochemical sensing of ofloxacin, pefloxacin and gatifloxacin* . *Talanta*, 2023, 255:124216.

[3] Liu Z, Wang Q, Xue Q, et al. *Highly efficient detection of ofloxacin in water by samarium oxide and β-cyclodextrin-modified laser-induced graphene electrode* . *Microchemical Journal*, 2023, 186:108353.

[4] Taha A M, Said R A M, Mousa I S, et al. *Simultaneous determination of ofloxacin and bromfenac in combined dosage form using four different spectrophotometric methods. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2022, 273:121066.

[5] Siddharthan A, Kumar V, Barooah N, et al. *Supramolecular interaction of ofloxacin drug with p-sulfonatocalix arene: Metal-ion responsive fluorescence behavior and enhanced antibacterial activity. Journal of Molecular Liquids*, 2023, 370:121047.

[6] Gupta K, Sharma D, Chawla P. *Simultaneous Estimation of Racecadotril and Ofloxacin by Reverse Phase High Performance Liquid Chromatography Method in Pharmaceutical Dosage Forms. Journal of Drug Delivery and Therapeutics*, 2019, 9(4):165-170.

[7] Silva R M S, Santos A M, Wong A, et al. *Determination of ofloxacin in the presence of dopamine, paracetamol, and caffeine using a glassy carbon electrode based on carbon nanomaterials* and *gold nanoparticles. Analytical Methods*, 2022, 14(39):3859-3866.

[8] Y. Zhang, A. Nsabimana, C. Han and L. Guo, et al. *Electrocatalytically active cobalt-based metal-organic framework with incorporated macroporous carbon composite for electrochemical applications. Journal of Materials Chemistry, A. Materials for energy and sustainability*, 2015, 3(2):732-738.

[9] Li Y, Zhai X, Liu X, et al. *Electrochemical determination of bisphenol A at ordered mesoporous carbon modified nano-carbon ionic liquid paste electrode. Talanta*, 2016, 148:362-369.

[10] Hang X, Xue Y, Cheng Y, et al. *From Co-MOF to CoNi-MOF to Ni-MOF: a facile synthesis of 1D micro-/nanomaterials. Inorganic Chemistry*, 2021, 60(17):13168-13176.

[11] Koventhan C, Chung Y C, Lo A Y, et al. *Development of a polyaniline/CMK-3/hydroquinone composite supercapacitor system. Materials Chemistry and Physics*, 2023, 297:127369.