Cobalt-cadmium bimetallic porphyrin coordination polymers for electrochemistry application

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Abstract. In this paper, we used tetra (4-carboxyphenyl) porphyrin (H₂TCPP) and metal cadmium, cobalt as reactants to synthesize metal porphyrin coordination polymers that they had different metal ratio. They were expressed as Co₁Cd₃TCPP, Co₁Cd₁TCPP, Co₃Cd₁TCPP, respectively. The results were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectrometer (ICP). Herein, a series of metal porphyrin coordination polymers has multiple metal active centers and constructs electrochemistry sensors. In order to increase the conductivity, multi-walled carbon nanotubes (MWCNTs) can be used to modify the electrodes. The polymer/MWCNTs/GCE electrode was studied by cyclic voltammetry and chronamperometry as sensor for sodium nitrite. The performance of Co₁Cd₁TCPP/MWCNTs/GCE electrode is best, the sensitivity for sodium nitrite is 350.95 mA M⁻¹ cm⁻² and the. The results indicate that metal porphyrin coordination polymers have excellent performance. It also enriches the application of metal porphyrin coordination polymer in electrochemistry sensor.

1. Introduce
The metal-organic frameworks (MOFs) are assembled by metal ions and organic ligands linked together through a coordination interaction and become a new kind of highly porous crystalline material [1]. Compared with the traditional inorganic porous materials, MOFs have a larger surface area, higher porosity, richer structure and function [2]. Therefore, metal-organic frameworks materials are widely used in gas adsorption and separation [3], catalytic reactions [4] and chemical sensing [5]. These applications typically require the incorporation of coordinative unsaturated metal ions in the framework to act as functional sites. The metal ligand has two different metal-binding sites, which can easily synthesize heteronuclear metal skeletons containing coordination unsaturated metal ions. Square planar building blocks based on tetraarylporphyrin, such as meso-tetra (4-pyridyl) porphyrin (TPyP) and meso-tetra (4-carboxyphenyl) porphyrin (TCP), have been used extensively as metal ligands in the synthesis of MOFs, with the goal of preparing catalytic materials [6]. Porphyrin ligands are used to synthesize heterogeneous metal frameworks and provide two different metal binding sites. The metal can be coordinated with the carboxyl or pyridine surrounding the porphyrin ring or the nitrogen of the porphyrin cavity. Cd (II) can be preferentially coordinated with carboxyl or pyridine around porphyrin due to the relatively large metal ion radius. This strategy has made some achievements in the synthesis of some mixed-metal frameworks using TPyP [7]. Co (II) has an empty d orbitals, making the transition metal prone to coordination. At the same time, the valence state of the metal cobalt changes
as a result of electron transfer processes, and the metal cobalt has excellent electrochemical performance.

Many articles have been published on the detection of small molecules using metal active centers, but there are less reportes that through different proportions of bimetallic synthesis of metal coordination polymer to detect small molecules. The coordination polymers can provide two metal active centers, and through experimental studies can find the best metal proportion of the metal coordination polymers for electrochemical sensing. In this paper, Co (II) and Cd (II) are coordinated with metal porphyrins which form a frame material to detect sodium nitrite.

2. Experiment section

2.1. Experimental materials
The cadmium chloride (CdCl$_2$ • 2.5H$_2$O, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The cobalt chloride (CoCl$_2$ • 6H$_2$O, AR) was purchased from Shanghai Reagent Plant (Shanghai, China). Multi-walled carbon nanotubes (MWCNTs, 97%) were purchased from Shenzhen Nanotechnology Technology Co., Ltd. (Shenzhen, China). Sodium nitrite (NaNO$_2$, AR) was purchased from Nanjing Chemical Reagent Factory (Nanjing, China). The disodium hydrogen phosphate (Na$_2$HPO$_4$, AR) and the sodium dihydrogen phosphate (NaH$_2$PO$_4$, AR) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. The 0.1 M phosphate buffer solution (PBS) was obtained from 0.1 M NaH$_2$PO$_4$ and 0.1 M Na$_2$HPO$_4$. All solutions were prepared with ultra-pure water purified by a Millipore-QSystem (ρ≥18.2 MΩ cm).

The polymers were characterized by X-ray diffraction (XRD, the Germany Brooke production diffractometer with Cu Kα radiation $\lambda$=1.5406Å, $\theta$=4s/step at room temperature ), transmission electron microscopy (TEM, H-7650, resolution: 0.204nm, magnification: high resolution mode: x200 ~ x600,000 and low magnification mode: x50 ~ x1,000) and inductively coupled plasma atomic emission spectrometer (ICP, US LEEMANLABS production, analytical elements: 73 elements, wavelength range 178 ~ 800nm, resolution: 0.006nm). The electrochemical measurements were carried out on a conventional three electrodes system with the glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode on a CHI660E electrochemistry workstation (Shanghai, Chenhua).

2.2. Synthesis of metal porphyrin coordination polymer
H$_2$TCPP were prepared according to the literature [8]. Then, H$_2$TCPP (80 mg, 0.1 mmol), CdCl$_2$ • 2.5H$_2$O (X$_1$ mmol) and CoCl$_2$ • 6H$_2$O (X$_2$ mmol) (X$_1$: X$_2$= 3: 1, 1: 1 and 1: 3) were dissolved in N, N-dimethylformamide (DMF) (6 mL) and H$_2$O (0.3 mL). The mixture was transformed into a Teflon-lined stainless steel autoclave having a capacity of 25 mL and heated to 150 °C for 48 h. Finally, the resulting precipitate was washed with DMF, alcohol and H$_2$O several times, and the product was dried at 50 °C in a vacuum.

2.3. Improved glassy carbon electrode
The glassy carbon electrode (GCE) was polished with alumina slurry and then ultrasonically cleaned in secondary distilled water to obtain mirror-like surface. Modified electrodes were fabricated as follows: First 6μL of suspension (5mg/mL) of MWCNTs was cast onto the GCE surface and dried at room temperature. Then 6μL of suspension (5mg/mL) of metal porphyrin coordination polymers were cast onto the surface of the GCE and dried in the air. Finally 2 μL of 1% nafion solution was dropped to cover the electrode surface. After drying in the air, the metal porphyrin coordination polymers/MWCNTs/GCE were obtained.
3. Results and discussion

3.1. XRD characterization of metal porphyrin coordination polymer

As it can be seen from figure 1, the XRD pattern of a series of metal porphyrin coordination polymers are compared with that of 1-Co (CCDC-865037) synthesized in literature. It is found that the peaks of (a) and (d) are in good agreement with each other. Through the comparison of (a), (b) and (c), it can be seen that the general position of the peak does not change, indicating that when the put into ratio is different, but we synthesized the structure of the metal porphyrin coordination polymers are same. It follows that the polymer composition changes when the metal is incorporated, but the spatial structure of the polymer is unchanged. So, we synthesized a series of metal porphyrin coordination polymers have the same structure. The diffraction peak of the metal coordination polymers were mainly due to their weak crystallinity.

![Figure 1. XRD pattern of metal porphyrin coordination polymer.](image)

3.2. TEM characterization of metal porphyrin coordination polymer

The morphology and size of the metal porphyrin coordination polymers were characterized by TEM. Figure 2 (a), (b), (c) represents the Co1Cd3TCPP, Co1Cd1TCPP and Co3Cd1TCPP polymers, respectively. It can be seen from the figure that the metal porphyrin coordination polymers present irregular particles with a width of 2 μm and a length of about 4 μm. It can be considered that the synthetized polymers do not present a specific morphology.

![Figure 2. TEM (Resolution: 0.204nm, magnification: high resolution mode: x200 ~ x600, 000 and low magnification mode: x50 ~ x1,000) diagram of metal porphyrin coordination polymers a: Co1Cd3TCPP, b: Co1Cd1TCPP and c: Co3Cd1TCPP.](image)

3.3. ICP characterization of metal porphyrin coordination polymer

In order to analyze the proportion of metal elements in the metal porphyrin coordination polymers, we tested the three kinds of metal porphyrin coordination polymers by ICP. The samples were pre-treated by dry ashing method and a small amount of samples were placed in a porcelain crucible and then placed in a muffle furnace. The temperature was gradually increased (100 °C/min) to 540 °C for 8 h in
the air atmosphere. The residue was dissolved with nitric acid at 7%. The cobalt and chromium were determined 228.615 nm and 228.802 nm, respectively. Table 1 shows the proportion of metal derived from ICP. It can be seen that the percentage of the metal atoms in the coordination polymer is consistent with the sample name.

| Sample name       | Atomic number ratio Co/Cd |
|-------------------|---------------------------|
| Co1Cd3TCPP        | 0.48                      |
| Co1Cd1TCPP        | 0.83                      |
| Co3Cd1TCPP        | 1.04                      |

### 3.4. CV testing of sodium nitrite

Figure 3 shows the CV detection of sodium nitrite for the metal porphyrin coordination polymer in PBS (pH=7.0). The peak at -0.79V is labeled as peak 1 and belongs to the oxidation peak of Cd(II)/Cd, the peak at 0.20V is labeled as peak 2 and belongs to the oxidation peak of MWCNTs, the peak at 0.80V is labeled as peak 3 and belongs to the oxidation peak of Co(III)/Co(II). The response of metal coordination polymer/MWCNTs/GCE to sodium nitrite was also studied. As it can be seen from the figure, when adding 0.5 mM sodium nitrite, the CV chart of the metal porphyrin coordination polymer/MWCNTs/GCE shows a significant increase in current in the range of -1~1V. It is indicating that the metal porphyrin coordination polymer/MWCNTs/GCE has an electrocatalytic activity for sodium nitrite. The response potential is the same as that of the metal porphyrin coordination polymer/GCE which does not add to the MWCNTs. However, the CV curve of MWCNTs/GCE in PBS with or without sodium nitrite does not significantly change, indicating that MWCNTs/GCE has no obvious catalytic effect on sodium nitrite.

![Figure 3](image)

**Figure 3.** Comparison of the CV curves of $5 \times 10^{-4}$ M NaNO$_2$ in PBS buffer solution (pH=7.0) as an electrochemical detection of the supporting electrolyte in metal porphyrin coordination polymer/MWCNTs/GCE and MWCNTs/GCE. The metal porphyrin coordination polymer represent that a is Co1Cd3TCPP, b is Co1Cd1TCPP, c is Co3Cd1TCPP.

### 3.5. I-t testing of sodium nitrite

The chronoamperometry (I-t) is more sensitive than cyclic voltammetry (CV). The CV showed that 0.85 V is the best potential, so sodium nitrite detection was carried out at this potential. Figure 4 to make the curve, the Co1Cd1TCPP has bigger current than Co1Cd3TCPP and Co3Cd1TCPP. Hence, the Co1Cd1TCPP/MWCNTs/GCE had the best performance for sodium nitrite detection. By the I-t detection at the optimum potential, with the concentration of sodium nitrite is increasing and the current value is also increasing. It is shown that the electrochemical sensor is responsive to sodium nitrite and that the response value of the current is linear relation to the increase in the concentration of
sodium nitrite. With the increase of sodium nitrite concentration, the response current of Co1Cd1TCPP / MWCNTs / GCE is also increasing, and the effect is obvious. The electrochemical sensor sensitivity is 350.95 mA M⁻¹ cm⁻² and the slope of the calibration curve is 0.9997.

![Graph showing electrocatalytic oxidation sensitivity of three metal porphyrin coordination polymers to sodium nitrite at optimum potential.](image)

**Figure 4.** Comparison of the electrocatalytic oxidation sensitivity of three metal porphyrin coordination polymers to sodium nitrite at optimum potential.

### 4. Conclusion

In this paper, a series of metal porphyrin coordination polymers was synthesized by solvent thermal method. The electrochemical properties and the detection properties of sodium nitrite were studied by cyclic voltammetry (CV) and chronoamperometry (I-t). The results show that the Co1Cd1TCPP/MWCNTs/GCE have better catalytic effect on sodium nitrite than the Co1Cd3TCPP/MWCNTs/GCE and the Co3Cd1TCPP/MWCNTs/GCE. And the metal porphyrin coordination polymer/MWCNTs/GCE have satisfactory stability. At the same time, the metal porphyrin coordination polymers also enrich the application of electrochemical sensors.

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