



A novel ratiometric electrochemical biosensor for sensitive detection of ascorbic acid



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ABSTRACT

In this work, a novel ascorbic acid (AA) ratiometric biosensor was prepared by using the PCN-333 (Al) metal-organic frameworks (MOFs) (PCN stands for porous coordination network) to encapsulate Ketjen black (KB) as catalyst for catalyzing oxidation of AA and thionine (Thi) as an internal reference signal simultaneously. The encapsulation of KB and Thi in the pores of PCN-333 (Al) MOFs not only improved efficiency of KB and Thi greatly because PCN-333 (Al) MOFs could effectively avoid the cohesion or aggregation of KB and Thi on electrode surface but also enhanced the stability of biosensors because they were immobilized in the pore firmly. Furthermore, PCN-333 (Al) MOFs could also selectively accumulate target analytes into their pores to enhance the selectivity of biosensors. The oxidation peak current of AA catalyzed by KB at -0.05 V increased with the increasing concentration of AA, while the oxidation peak current of Thi at -0.24 V kept constant, which resulted in a novel ratiometric biosensor for AA detection. The ratiometric biosensor exhibited a wider linear range from 14.1 ± 0.2 to $(5.5 \pm 0.1) \times 10^3 \mu\text{M}$ ($R^2 = 0.998$) and a lower detection limit of $4.6 \pm 0.1 \mu\text{M}$ with high accuracy, selectivity, reproducibility and sensitivity. The ratiometric electrochemical approach is not only a new method for AA detection but also opens a new way for sensitive detection of other analytes.

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1. Introduction

Ascorbic acid (AA), also called vitamin C, is a vital vitamin in human body and it also exists widely in fruit, animal feed, vegetables, serum, central nervous system, etc [1–3]. Moreover, the AA has also been used for the treatment of mental illness, cancer, common cold, infertility and for improving the immunity because the AA plays a key role in biological metabolism [4–8]. Accordingly, it is very important to detect AA in various samples. However, the selectivity and sensitivity of the detection of AA was often very poor due to the interference of coexisted dopamine (DA) and uric acid (UA). So it still is very important and urgent to develop a sensitive and selective method for the reliable determination of AA.

Recently, many methods have been developed for the sensitive and selective detection of AA such as chromatography [9,10], fluorescence spectroscopy [11], UV–vis absorbance spectroscopy [12], electrochemical sensor [4,13–15] and so on. Among these methods, electrochemical sensor has attracted more attention due to its

simplicity, low cost and easy miniaturization [16–19]. However, the overlapping of the oxidation peaks of AA, DA and UA at traditional electrodes makes the sensitive and selective detection of AA very difficult. Accordingly, some special carbon-based nanomaterials modified electrodes have been developed such as graphene, carbon nanotubes, carbon nanofiber, hollow nitrogen-doped carbon microspheres, Ketjen black (KB) and activated carbons, etc [20–24]. Although the oxidation potential of AA at these carbon-based nanomaterials modified electrodes could be separated from the UA and DA, these carbon-based nanomaterials are easy to aggregate on electrode surface and take off from electrode surface to result in a low sensitivity and a poor stability. Therefore, how to enhance the stability and dispersion of nanomaterials on the electrode surface for improving the performance of sensor is still a challenge.

Presently, ratiometric electrochemical sensors has attracted the extensive attention owing to its good self-calibration, lower detection limit, and the ability to overcome the environmental and personal factors and thus enhances the reproducibility greatly [25–31]. Generally, in the ratiometric electrochemical sensors, two kinds of electroactive substances with different redox potentials were co-immobilized on electrode surface. One electroactive substance was used as an internal reference signal and another one was used for the detection of analytes or the two kinds of electroac-

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tive substance was used to record the signal simultaneously, which could improve the sensitivity and reliability. For example, Yuan Ruo et al. has developed a ratiometric electrochemical method to detect lipopolysaccharide by using the Cu-based metal-organic frameworks (MOFs) as signal recognition part and ferrocene as an internal reference signal [29]. Wei et al. developed a ratiometric electrochemical sensor to detect AA by using the thionine (Thi)/Ketjen black (KB) nanocomposites dropped on the surface of glassy carbon electrode (GCE) [32]. Although the ratiometric electrochemical sensor could selectively detect AA, the Thi and KB were just only physically mixed, which made the components easy fall off from the electrode surface to result in a poor performance.

Herein, we prepared a PCN-333 (Al) MOFs (PCN stands for porous coordination network) to encapsulate the KB and Thi by a simple one-step method for AA sensing. The redox peak of Thi occurred at -0.24 V was used as an internal reference signal and the KB was used to catalyze the oxidation of AA at -0.05 V to result in a novel ratiometric biosensor for AA detection (Fig. 1). The MOFs has been used to encapsulate enzyme, nanomaterials and small molecules for various applications owing to their high porosities and tunable pore size [33–40]. The encapsulation not only improved efficiency of materials greatly because MOFs could effectively avoid the aggregation of materials on electrode surface but also enhanced the stability of sensors because they were immobilized in the pore firmly. Furthermore, MOFs could also selectively accumulate target analytes into their pores to enhance the selectivity of sensors. Accordingly, the ratiometric biosensor exhibited good performance for AA detection.

2. Experimental

2.1. Chemicals and materials

The KB was purchased from Shanghai Cuike Chemical Co. Ltd (Shanghai, China). Aluminium trichloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2 , AR, 30 wt.% in H_2O) and N, N-dimethyl formamide (DMF, AR) were obtained from Aladdin. The 4, 4', 4''-s-triazine-2, 4, 6-triyl-tribenzoic acid (H_3TATB , 95%) and trifluoroacetic acid (TFA, 99%) were purchased from Sigma-Aldrich. The Thi was purchased from Alfa-Aesar. The AA, glucose, mannose, sucrose, urea, NaCl, KCl, cysteine, UA, DA and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The 0.2 M phosphate buffer solution (PBS) was obtained from 0.2 M NaH_2PO_4 and 0.2 M Na_2HPO_4 . All solutions were prepared with ultra-pure water purified by a Millipore-Q System ($\rho \geq 18.2 \text{ M}\Omega \text{ cm}$).

2.2. Preparation of PCN-333 (Al) MOFs-KB-Thi nanocomposites

The PCN-333 (Al) MOFs-KB-Thi nanocomposites were prepared as follows. The H_3TATB (10 mg) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (40 mg) were dissolved in 2 mL DMF and then the 200 μL TFA was added into the above solution. Then the KB (8 mg) and Thi (16 mg) were subsequently added to the mixed solution. After that, the solution was heated at 135°C in an oven for 2 days. The formed nanocomposites were rinsed thoroughly with DMF and water for three times. The PCN-333 (Al) MOFs, PCN-333(Al) MOFs-KB and PCN-333 (Al) MOFs-Thi were also prepared by the same procedures. The resulted nanocomposites were dispersed in Milli-Q water with the concentration of 5 mg mL^{-1} for further experiments.

2.3. Preparation of PCN-333 (Al) MOFs-KB-Thi modified GCE

The bare GCE was firstly polished with 0.3 μm and 0.05 μm , ultrasonically cleaned in pure water and ethanol for 5 min, respectively and then dried under a highly pure N_2 stream for further

experiment. To achieve the modified electrode, the 7.0 μL PCN-333 (Al) MOFs-KB-Thi suspension was dropped onto the surface of the polished GCE electrode and then dried in air. Finally, the modified GCE was rinsed by using 0.2 M PBS (pH 7.0) to remove the weakly absorbed materials from modified electrode and the resulted modified GCE was defined as PCN-333 (Al) MOFs-KB-Thi/GCE.

2.4. Instrumentations

All electrochemical experiments were carried out using a CHI 760D electrochemical workstation (Shanghai, China). A three-electrode system was used including a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the PCN-333 (Al) MOFs-KB-Thi/GCE, PCN-333 (Al) MOFs-KB/GCE or PCN-333 (Al) MOFs-Thi/GCE as the working electrode. Cyclic voltammograms (CVs) were operated in 0.2 M N_2 -saturated PBS (pH 7.0) or 0.1 M N_2 -saturated KCl solution containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at room temperature. Electrochemical impedance spectroscopy (EIS) was performed in 0.1 M KCl solution containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at open circuit potential in the frequency range from 0.01 Hz to 10^5 Hz with the amplitude of 5 mV. Differential pulse voltammetry (DPV) was performed in 0.2 M N_2 -saturated PBS (pH 7.0) with amplitude of 50 mV and pulse width of 0.2 s. Scanning electron microscopy (SEM) images were performed using a HITACHI S-3400N SEM at an accelerating voltage of 15 kV N_2 adsorption-desorption isotherm measurements were carried out using a BELSORP-mini II instrument at the liquid nitrogen temperature (77 K).

3. Results and discussion

3.1. Characteristics of PCN-333 (Al) MOFs-KB-Thi nanocomposites

The prepared PCN-333(Al) MOFs and PCN-333 (Al) MOFs-KB-Thi MOFs nanocomposites were carefully characterized by SEM. As shown in Fig. 2A, the SEM image of PCN-333 (Al) MOFs (Fig. 2A) showed an octahedral structure with a diameter of 1 μm , and some irregular structures also appeared. Compared to that of PCN-333 (Al) MOFs, the SEM image of PCN-333 (Al) MOFs-KB-Thi (Fig. 2B) showed lots of small particles grew on the surface of irregularly octahedral PCN-333 (Al) MOFs-KB-Thi. The small particles might be ascribed to the nanosized KB which absorbed on the surface of PCN-333 (Al) MOFs-KB-Thi. The N_2 adsorption-desorption isotherms were also utilized to characterize the PCN-333 (Al) MOFs-KB-Thi nanocomposites. As shown in Fig. S1 (Supporting information), the Brunauer-Emmett-Teller (BET) surface area was found to be $128.4 \text{ m}^2/\text{g}$ for the PCN-333 (Al) MOFs-KB-Thi nanocomposites, which is much smaller than the PCN-333 (Al) MOFs ($1550.7 \text{ m}^2/\text{g}$). The results clearly demonstrated that the KB and Thi were not only absorbed on the surface of PCN-333 (Al) MOFs but also successfully encapsulated into the pores of PCN-333 (Al) MOFs.

The CVs was used to characterize the PCN-333 (Al) MOFs-KB-Thi/GCE in 0.1 M KCl solution containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as shown in Fig. 3A. For the PCN-333 (Al) MOFs/GCE (Fig. 3A, curve b), a pair of typical redox peaks of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ appeared. However, the peak current obviously decreased and the peak-to-peak potential separation (ΔE_p) increased significantly as compared to the bare GCE (Fig. 3A, curve a), indicating that the PCN-333 (Al) MOFs have an obvious hindering to the electron transfer of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ owing to their poor electrical conductivity. The peak current increased and the ΔE_p decreased after the GCE modified with PCN-333 (Al) MOFs-KB-Thi nanocomposites (Fig. 3A, curve c) due to the high electrical conductivity of KB to promote the electron transfer of $[\text{Fe}(\text{CN})_6]^{3-/4-}$.

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