



# Facile electrosynthesis of nickel hexacyanoferrate/poly(2,6-diaminopyridine) hybrids as highly sensitive nitrite sensor

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## ABSTRACT

In this study, a simple and sensitive method for the determination of nitrite ( $\text{NO}_2^-$ ) in environmental and food samples by amperometry with nickel hexacyanoferrate/poly(2,6-diaminopyridine) (NiHCF/PDAP) hybrids modified electrode was developed. The NiHCF/PDAP hybrids prepared via a facile one-step electrosynthesis method exhibited significantly high sensitivity and wide linear range for the determination of nitrite due to the high electrocatalytic activity of NiHCF and the preconcentration ability of PDAP in acidic conditions. In addition, the as-prepared NiHCF/PDAP also showed high selectivity with no interferences from other anions, high stability and reproducibility in the determination of nitrite. Finally, the developed hybrids were applied in the determination of nitrite in tap water, lake water and ham sausage samples, and the results demonstrated its potential as a sensitive and selective electrochemical sensor for nitrite.

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## 1. Introduction

It is well known that nitrite ( $\text{NO}_2^-$ ) can prevent bacteria growth, and it is commonly used in food technology for curing meat as food preservatives. However, excess level of nitrite in the blood will lead to the oxidation of Fe(II) to Fe(III) within the hemoglobin molecules which may be fatal [1,2], and thus the World Health Organization (WHO) has set daily maximum intake of nitrite as 0.07 mg of nitrite ion/kg of body weight [3]. Moreover, the reaction of nitrite with secondary amines and amides can yield highly carcinogenic *N*-nitrosoamines [4]. Therefore, quantitative and sensitive determination of nitrite in food and environmental samples is of great importance. A number of methods have been developed to date for nitrite determination such as high-performance liquid chromatography (HPLC) [5], spectrophotometry [6], fluorometry [7], colorimetry [8] and electrochemistry [9–11]. Among them, electrochemical method is especially favorable for nitrite determination due to its fast response, high sensitivity, simple use and low cost. However, the determination of nitrite with bare electrode has rarely been reported [12], because several species can poison the electrode surface and consequently decrease the accuracy and

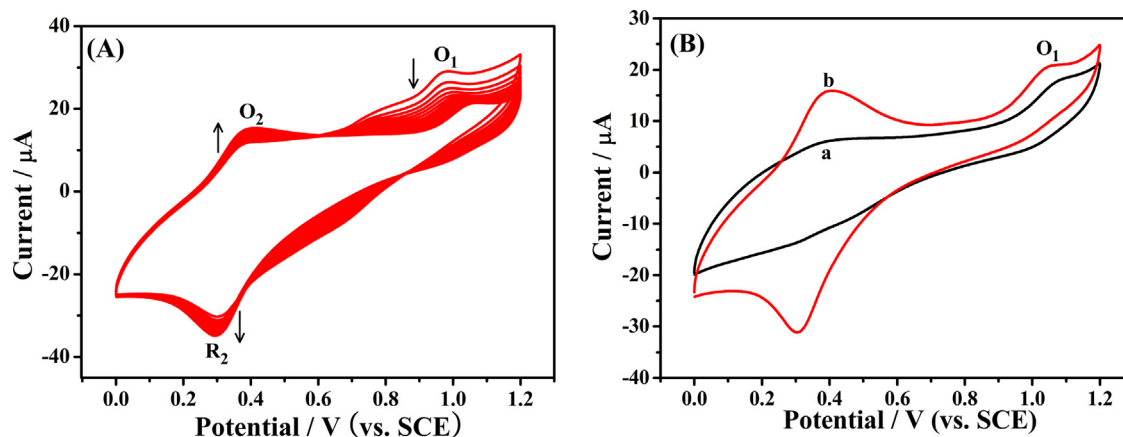
sensitivity. Fortunately, the use of chemically modified electrodes can effectively improve the detection sensitivity [13–15].

Conducting polymers (CPs) have received a great deal of attention due to their intriguing chemical and physical properties, and the past decades have witnessed the applications of CPs as suitable materials for the construction of electrochemical sensors with attractive features such as ease of synthesis, high sensitivity and fast response time [16–18]. Poly(2,6-diaminopyridine) (PDAP) is a kind conducting polymers, which can be synthesized via chemical [19] or electrochemical [20,21] oxidative polymerization, and the applications of PDAP for ascorbic acid and hydrogen peroxide sensing have also been reported by Cao et al. [22,23]. In fact, PDAP is especially advantageous for the sensitive determination of anions, since the amino groups ( $-\text{NH}_2$ ) on PDAP may be protonated in acidic conditions and consequently anions can be pre-concentrated to the surface of PDAP via electrostatic attractions.

Transition metal hexacyanoferrates (MHCFs) such as nickel hexacyanoferrate (NiHCF), cobalt hexacyanoferrate (CoHCF) and palladium hexacyanoferrate (PdHCF) are derived from the Prussian blue family [24–26], and they have received increasing attention as a group of excellent electron transfer mediators [27]. For example, NiHCF modified electrodes have been used in electroanalysis [28] and sensing of nitrite [29]. More importantly, most of the MHCFs can be easily deposited on the electrode surface via a simple and

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**Fig. 1.** (A) Cyclic voltammograms recorded during the growth of NiHCF/PDAP hybrids on GCE for 15 cycles at a scan rate of  $100 \text{ mV s}^{-1}$ . (B) The 15th cycle on the cyclic voltammograms for the electrosynthesis of PDAP (a) and NiHCF/PDAP (b) on GCE.

green electrochemical method, producing controllable and well tuned nanostructures of the electrodeposited MHCFs [30].

Recently, some nano hybrids have been synthesized and successfully used in various fields such as photocatalysis [31,32] and sensing [33,34]. In the present work, a highly sensitive and selective nitrite sensor based on NiHCF/PDAP hybrids is facilely prepared by a one-step strategy. The preconcentration of nitrite on the hybrids is achieved via the electrostatic attractions between the protonated  $-\text{NH}_2$  ( $-\text{NH}_3^+$ ) on PDAP and the negatively charged nitrite, and the electrocatalytic oxidation of nitrite occurs with the aid of  $\text{Fe(III)(CN)}_6/\text{Fe(II)(CN)}_6$  couple from NiHCF in the hybrids. Due to the synergistic effects of PDAP and NiHCF, the as-prepared nitrite sensor provides a highly sensitive, reproducible and fast amperometric determination of nitrite while effectively avoids interferences from other anions. Finally, the developed hybrids-based sensor is successfully applied in the determination of nitrite in tap water, lake water and ham sausage samples.

## 2. Experimental

### 2.1. Reagents and apparatus

2,6-Diaminopyridine, nickel sulfate ( $\text{NiSO}_4$ ) and potassium ferriyanide ( $\text{K}_3\text{Fe(CN)}_6$ ) were purchased from Aladdin Chemicals Reagent Co., Ltd. (Shanghai, China). Sodium nitrite ( $\text{NaNO}_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), sodium chloride ( $\text{NaCl}$ ), sodium hydroxide ( $\text{NaOH}$ ), sodium alginate (SA), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) were received from Sinopharm Chemical Reagent Co., Ltd. (SCRC, China). All solutions were prepared with ultrapure water of  $18.2 \text{ M}\Omega$  (Milli-Q, Millipore).

The morphologies of NiHCF/PDAP and PDAP were recorded on a Supra55 field-emission scanning electron microscope (FESEM, Zeiss, Germany). The Fourier transform infrared (FT-IR) spectra of NiHCF/PDAP and PDAP were recorded with a FTIR-8400S spectrometer (Shimadzu, Japan). All the electrochemical experiments including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), differential pulse voltammetry (DPV) and chronoamperometry were carried out on a CHI 660E electrochemical workstation.

### 2.2. Preparation of NiHCF/PDAP-based nitrite sensor

The one-step preparation of NiHCF/PDAP hybrids was carried out in a conventional three-electrode cell consisting of glassy carbon electrode (GCE, 3 mm in diameter) as the working elec-

trode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was 25 mL of 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution containing 2 mM 2,6-diaminopyridine, 2 mM  $\text{K}_3\text{Fe(CN)}_6$ , 2 mM  $\text{NiSO}_4$  and 0.25 M  $\text{Na}_2\text{SO}_4$ , and the NiHCF/PDAP hybrids were directly deposited onto the surface of GCE by CV in the potential range from 0 to 1.2 V at a scan rate of  $100 \text{ mV s}^{-1}$ . The electrolysis was finished after 15 repeated cycles, and the resulting NiHCF/PDAP hybrids were rinsed thoroughly with ultrapure water. For control experiments, PDAP was also synthesized by CV in 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution containing 2 mM 2,6-diaminopyridine and 0.25 M  $\text{Na}_2\text{SO}_4$ .

### 2.3. Electrochemical determination of nitrite with NiHCF/PDAP hybrids

The electrochemical responses of nitrite at the NiHCF/PDAP hybrids were investigated by CV, DPV and chronoamperometry, and all the electrochemical experiments were carried out in a three-electrode system with NiHCF/PDAP modified GCE as the working electrode, a platinum foil and a SCE as the counter and reference electrodes, respectively. The chronoamperometric measurements in response to nitrite were carried out at an applied potential of 0.8 V in 0.1 M phosphate buffer saline (PBS) of pH 4.0 under continuous stirring.

## 3. Results and discussion

### 3.1. One-step electrosynthesis of NiHCF/PDAP hybrids

Fig. 1A shows the CVs during the electrosynthesis of NiHCF/PDAP hybrids at a scan rate of  $100 \text{ mV s}^{-1}$  for 15 cycles. There is an irreversible oxidation peak ( $\text{O}_1$ ) at around 0.98 V on the forward scan of the first cycle, which is attributed to the oxidation of 2,6-diaminopyridine. However, the peak current is decreased in the subsequent cycles, which is accompanied by the appearance of a pair of redox peaks ( $\text{O}_2/\text{R}_2$ ) at 0.40/0.31 V. To understand the redox peaks of  $\text{O}_2/\text{R}_2$ , the 15th cycle on the CVs for the electrosynthesis of NiHCF/PDAP and PDAP is also recorded for a comparison (Fig. 1B). The CVs for the synthesis of PDAP display a small redox peaks at around 0.39/0.31 V (curve a), due to the formation of PDAP [35]; meanwhile, the CVs for NiHCF/PDAP electrosynthesis also show a significantly enhanced redox peaks at around 0.39/0.31 V (curve b), which is assigned to the redox of  $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$  couple in NiHCF [25,36]. This comparison clearly indicates that the redox peaks of  $\text{O}_2/\text{R}_2$  in Fig. 1A are attributed to the superposition of redox peaks of PDAP and redox peaks of  $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ , and obvi-

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