



Covalent anchoring of cobalt hexacyanoferrate particles on graphitic carbon: A simple and renewable robust pellet electrode as an electrochemical interface for amperometric quantification of sulfite



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ABSTRACT

A simple strategy has been proposed for the covalent anchoring of cobalt hexacyanoferrate (CoHCF) particles on graphitic carbon substrate using *p*-phenylenediamine as a linker molecule. The covalent anchoring was confirmed by X-ray diffraction, Fourier transform infrared spectroscopy and electrochemical studies. A robust pellet electrode was fabricated using CoHCF particles modified graphitic carbon and it has been applied in the electrocatalytic oxidation of sulfite. The proposed sensor showed a linearity in the concentration range 4–128 μM of sulfite with a limit of detection (LOD) 1.7 μM and limit of quantification (LOQ) 5.8 μM . Proposed sensor has been successfully applied to measure sulfite levels from a variety of food sample matrices. The results obtained by the proposed electrochemical sensor have been compared with the iodimetric method.

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1. Introduction

Polynuclear mixed valence compounds are well known as electron transfer mediators. Several articles have been reported detailing the electrochemical behavior of transition metal hexacyanoferrates (MHCFs) due to their excellent electrochemical sensing property [1–3]. Electrochemical redox reaction paralleled by the charge balance is facile when the crystal structure of the probe is open enough to intercalate and deintercalate alkali cations of the supporting electrolyte. Cobalt hexacyanoferrate (CoHCF) is very akin to iron hexacyanoferrate in this regard [4]. Different strategies have been used to modify the electrode surface with CoHCF. Among them, ‘seed-mediated’ method [5], physical immobilization [6], screen printing [7], electrochemical deposition [8] and some uncommon methods like ‘iron (III) oxide core – CoHCF shell’-modified carbon paste electrode (CPE) [9] are significant ones. In another strategy, aluminium oxide was used as a template to deposit the CoHCF in multistep [10]. Chitosan was used to put together carbon nanotubes (CNTs) and CoHCF

nanoparticles to observe the amplified electrochemical signal [11]. CoHCF modified electrodes have been extensively used in sensing and quantification of different analytes like sulfite, cysteine, ascorbic acid & dopamine, thiosulphate and heavy metal ions [3,9,10,12,13]. CoHCF loaded onto the electrode through the physically immobilized amine and it has been applied in the sensing of anisole [14]. This kind of derivatization can’t be used to renew the electrode surface and surface cleaning is very difficult. Modified silica was used as a template to prepare the CoHCF nanorods on glassy carbon electrode (GCE) by Berrettoni et al. Such CoHCF nanorods retained the initial response even after a number of cycles [15].

Various carbon substrates were tagged to CoHCF to improve the electron charge transfer rates. Composites of CoHCF with graphene [16–18], CNTs [19–22] and on carbon cloth [23] have been reported recently for the determination of various analytes. The addition of carbon substrates found to be advantageous and improved the analytical figures of merit. But in most of such reports, CoHCF and carbon substrates were physically combined. Then it is placed on glassy carbon electrode by drop casting or used in the form of CPE. However the modifier leaching from the electrode surface is very common in such cases, which in turn affect the reproducibility and reliability of the method. Hence, we aimed to overcome this problem by chemically derivatizing the carbon substrate with CoHCF. This chemical modification has been achieved by anchoring

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p-phenylenediamine (ppda) onto the graphitic carbon and used as a linker molecule. Taking the advantage of the presence of lone pairs on the ppda, cobalt ions were datively introduced onto it. Then hexacyanoferrate ions were reacted with cobalt ions on the graphitic carbon. Even though CPE provides the renewable surface, binders used hinder the electrode kinetics and the performance of the electrode will diminish with time [24]. Inspired by the long storage stability, surface renewability and better electrode kinetics [25,26], binderless pellet electrode has been constructed using the CoHCF derivatized graphitic carbon. There by the disadvantages such as modifier leaching, hindered electrode kinetics has been successfully overcome.

Sulfite is a well known preservative and can be found in many food and beverage products. Before 1986, sulfite was considered safe for consumers. Later, understanding the adverse effects, its declaration on the products was made mandatory [27]. Though sulfite is helpful in preserving food products, its content should be restricted to upheld the safety of the consumers. Therefore, quantification of sulfite in food and beverages is of prime importance in order to understand their quality. Several analytical methods have been reported for sulfite quantification at trace level. Among these, the methods based on spectrophotometry, spectrofluorimetry and electrochemical methods found widespread use in the measurement of sulfite [28–37]. Among them, electrochemical methods found to be simple and easily adaptable for real sample analysis. In recent years chemically modified electrodes using a variety of modifier molecules incorporated into carbon substrates have been the focus of interest in sensor technology for target analytes.

Here in, we propose a simple strategy to covalently derivatize the graphitic carbon with CoHCF particles. The composite was compressed into pellet to construct a robust pellet electrode. The surface of this robust electrode is quite stable and its surface can be renewed easily by simple mechanical polishing. The applicability

of the designed electrode was tested by sulfite quantification from different sample matrices.

2. Experiment

2.1. Apparatus

Cyclic voltammetry and amperometric experiments were carried out using an electrochemical work station (CH Instruments, Texas, USA model: CHI-660D) in a standard three-electrode cell. A robust pellet electrode of 5 mm diameter was used as a working electrode after compressing the chemically modified graphitic carbon particles into a pellet and fabricating it as an electrode. A Pt wire of 1 mm diameter and Ag/AgCl (saturated KCl) acted as counter and reference electrodes respectively. Unless otherwise stated, all the mentioned potentials are measured against Ag/AgCl reference electrode. Infrared (IR) spectra were recorded using a Bruker Alpha-T Fourier transform infrared (FTIR) Spectrometer (Diamond crystal ATR mode, resolution 4 cm^{-1} , range $400\text{--}4000\text{ cm}^{-1}$). The powder XRD measurements were performed using PANalytical X'pert PRO X-ray diffractometer with graphite monochromatized Cu K α radiation source ($\lambda = 1.541\text{ \AA}$).

2.2. Chemicals and reagents

Sodium sulfite (2 mM): Prepared by dissolving 0.0252 g of anhydrous Na_2SO_3 in 100 mL of water.

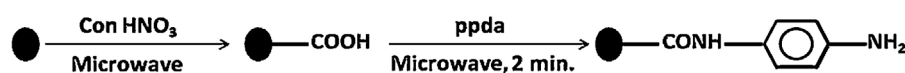
Cobalt chloride (30 mM): Prepared by dissolving 0.711 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of methanol.

Potassium hexacyanoferrate (30 mM): Prepared by dissolving 0.130 g of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 100 mL of water.

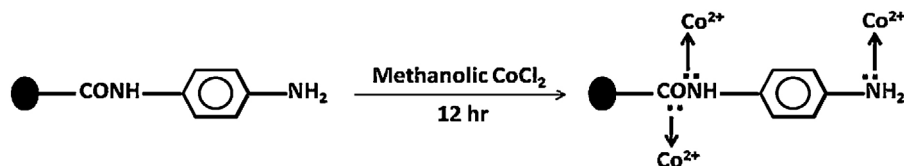
Potassium nitrate (0.5 M): Prepared by dissolving 20.2 g of KNO_3 in 100 mL water.

Tetrabutylammoniumhexacyanoferrate ($\text{N}(\text{C}_4\text{H}_9)_4_3[\text{Fe}(\text{CN})_6]$): Was prepared by following the reported procedure [38]. In brief,

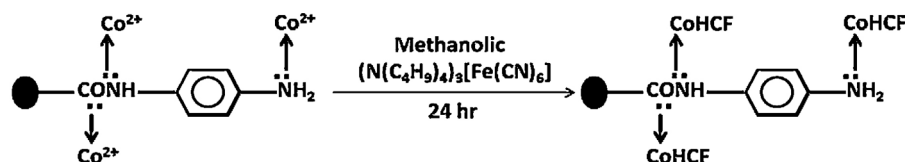
I. Functionalization of graphitic carbon with ppda through oxidation and amidation reactions



II. Anchoring of cobalt ions onto ppda functionalized graphitic carbon



III. Anchoring of cyano-bridged hexacyanoferrate



Scheme 1. Schematic representation of a stepwise covalent modification of graphitic carbon with cobalt hexacyanoferrate particles.

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