

Modified electrode using multi-walled carbon nanotubes and a metallopolymer for amperometric detection of L-cysteine



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ABSTRACT

This work describes for the first time the modification of a glassy carbon electrode with a hybrid material formed by the dispersion of multi-walled carbon nanotubes in the metallopolymer P4VP-Fe(CN)₅. The reversible redox couple of the material was formed at relatively low overpotential and showed a good electrocatalytic activity toward cysteine electrooxidation. The cathodic shift of the oxidation process for the modified electrode was 500 mV compared to the bare glassy carbon electrode. The rate constant (k_{obs}) for the chemical reaction between the redox mediator and cysteine was found to be $8.95 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$. The analytical curve was found to be linear from 20.5 up to 151 nmol L^{-1} , with a sensitivity of $0.996 \text{ nA L nmol}^{-1}$ and response time of 0.1 s.

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1. Introduction

The carbon nanotubes (CNT) are structures with demonstrated capability of favoring electron transport from the electroactive layer to the electrode surface owing to its high charge mobility [1]. CNT associated with redox mediators impart advantages once incorporated into analytical platforms for sensing not only of Cys [2–4], but also of hydrogen peroxide [5], glucose [6] and others [7,8]. The challenge in coating an electrode with CNTs is to achieve a good dispersion [9] since the highly hydrophobic walls tend to hold CNTs together in bundles or in microscopic aggregates via van der Waal forces. Therefore, the outermost walls must be functionalized to improve CNT wettability. Soft non-covalent functionalization methods are preferable over oxidizing ones when the electronic conductivity is wanted to be preserved [10]. Usually, CNT are initially dispersed by a dispersing agent that can be a low-molecular weight surfactant like sodium dodecylsulfate [11] and pyrene derivative [12], conjugated polymer [13] or a nitrogen-containing polymer such as polyethyleneimine [2], poly(L-lysine)

[3], chitosan [8] or poly(4-vinylpyridine) (P4VP) [4]. Polymers are advantageous in electrochemical sensor production due to its film-forming ability, which makes a thin homogeneous coating more likely. The redox mediator is anchored in a second step by dipping the CNT/dispersant-covered electrode into a solution of the electroactive species.

Herein we report an alternative assembly method where the redox mediator is already bound to the dispersing polymer via coordination. Redox metallopolymer such as that formed by P4VP bearing a coordination compound with known redox properties like ruthenium or osmium complexes [14,15] and pentacyanoferrate [15,16] have long been used for electrode modification. However, reports on the use of pyridyl-pendant polymer complexed with pentacyanoferrate together with CNT for electrochemical sensing are scarce [6]. Parra-Alfambra and coworkers used a pyridyl-derivatized chitosan to bind pentacyanoferrate, similarly as described by Rodrigues et al. [17]. These types of materials appear promising for monitoring substances of biological interest, such as for, example cysteine.

L-Cysteine (Cys) is a sulphur-containing amino acid with critical importance for many biological functions. Although it can be synthesized *in vivo* under normal physiological conditions via trans-sulphuration reaction between L-methionine and L-serine [18], it must be ingested at some circumstances, as in the case of premature neonates [19]. Cys is present ubiquitously in protein structures where its sulphhydryl group can be found free (pK_a 8.0),

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forming disulphide bridges (cystine) or complexed with metal ions in active sites of several proteins and enzymes, such as chloroperoxidase, cytochrome P450 and alcohol dehydrogenase [20]. Abnormal levels of Cys are related to the development of pathological conditions like Parkinson's and Alzheimer's disease, leukemia, diabetes, liver disorders, among others [21].

As a consequence of the importance of Cys, several determination methods have been developed. Spectroscopic methods usually need derivatization of Cys to introduce a chromogenic or fluorogenic moiety [22,23]. Detection through high performance liquid chromatography might take more than 10 min, reaches detection limits in the order of femtomol, but also require derivatization for fluorescence detection [24]. On the other hand, electrochemical methods have the advantages of rapid response, relative low cost, simplicity of the instrumentation and high sensitivity which make them more suitable for practical uses. Cys, as well as other sulphur-containing molecules, have been determined by various electrochemical techniques such as amperometry, biamperometry, voltammetry and pulsed electrochemical detection [25].

The major problem that must be circumvented for electrochemical determination of Cys and other thiols is the high overpotential required in most conventional electrodes (Pt and glassy carbon). Electrochemical oxidation at such highly positive potentials causes oxide formation at the electrode surface and significantly reduces the detection selectivity. Our sensing system employs the metallopolymer formed with P4VP and pentacyanoferrate, whose ability to efficiently disperse CNT. Owing to the solvatochromic properties of the complex [26], it is possible to infer spectroscopically the hydrophobicity of the chemical environment where it is placed [27]. The dispersion procedure the metallopolymer yields samples with 0.6 mg/mL of MWCNT stable for at least 30 days. Aligning the CNT-dispersion capability of the free pyridyl groups with the electrochemical properties of the pyridyl groups complexed with pentacyanoferrate, we describe an amperometric sensor for L-cysteine with a high rate constant for the chemical reaction.

2. Experimental

2.1. Chemicals and materials

All reagents were used as received from commercial sources, with no further purification. The multi-walled carbon nanotubes

(95 wt% purity, 10–40 nm external diameter, 5–20 μm length) were acquired from CNT Co., Ltd., Incheon, Korea. Sodium nitroprusside (99%) was purchased from Merck, Darmstadt, Germany. Poly(4-vinylpyridine) (99%, $M_w = 160,000$), ammonium hydroxide (28%) and L-cysteine (Cys) were acquired from Sigma–Aldrich, St. Louis, USA. Disodium phosphate (Na_2HPO_4), monosodium phosphate (NaH_2PO_4), potassium chloride (KCl) and ethanol were acquired from Synth, São Paulo, Brazil. The solutions were prepared by using water purified in a Milli-Q Millipore system and the pH values of the buffer solutions were determined with a Corning pH/lon Analyser model 350. Standard solutions were daily prepared by appropriate dilution of the stock solutions with deionized water.

2.2. Synthesis of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$

Sodium aminopentacyanoferrate(II) has a labile ammonia ligand that was planned to be displaced by the pendant pyridyl moieties of P4VP. The procedure was based on sodium nitroprusside in concentrated ammonium hydroxide, as described elsewhere.[28]

2.3. Synthesis of the metallopolymer $[\text{Fe}(\text{CN})_5\text{P4VP}]_{10}$

Initially, 5.0 mL of a poly(4-vinylpyridine) stock solution in ethanol with a concentration of 380 mmol L^{-1} of the polymer repeating unit (40 g L^{-1} of P4VP) is placed in a round-bottom flask and is deaired by flowing nitrogen for 15 min. An aliquot of 1.550 mL of a 122 mmol L^{-1} aqueous solution of $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)]\cdot 3\text{H}_2\text{O}$ is added, and the mixture is stirred at room temperature for 2 h. The aliquot volume was chosen to achieve the desired polymer repeating unit/pentacyanoferrate molar ratio of 10. During the stirring, 1.6 mL of deaired water was added to homogenize the forming metallopolymer solution. After that, the flask's atmosphere was saturated with nitrogen and it was stored at 8°C in order to slow decomposition.

2.4. Production of MWCNT suspensions

To obtain the dispersion of MWCNTs/ $[\text{Fe}(\text{CN})_5(\text{P4VP})_{10}]$, the following procedure was employed: $38.4\ \mu\text{L}$ of a metallopolymer solution recently prepared as described in Section 2.2 was added to 3.453 mL of water:ethanol, 60:40 molar ratio and subsequently

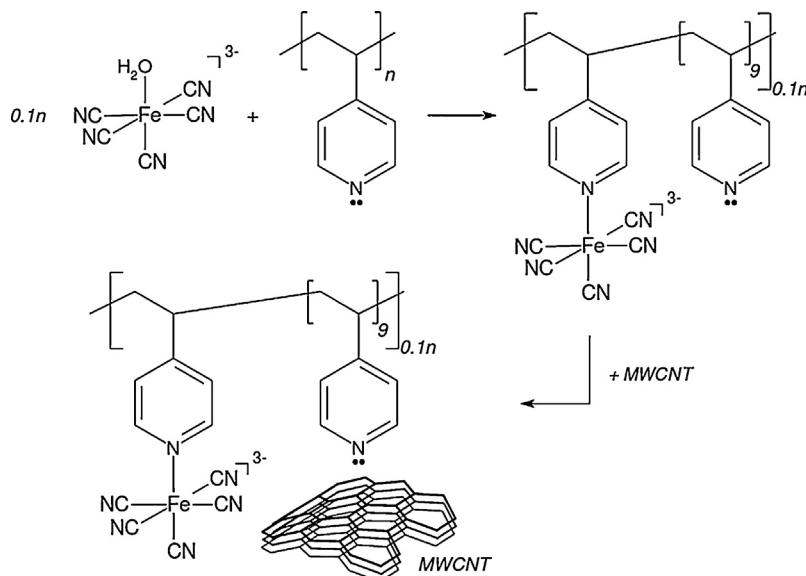


Fig. 1. Scheme of the metallopolymer molecular blocks. Metal-containing chain units and the organic block as the metal-free chain segments.

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