



Electrocatalytic oxidation of sulfide and electrochemical behavior of chlorpromazine based on organic–inorganic hybrid nanocomposite



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ABSTRACT

For the first time, this work describes the electrochemical behavior of chlorpromazine as a modifier on the surface of electrodes. The electrochemical properties of chlorpromazine in the silica nanoparticles/chlorpromazine/Nafion (SNPs/CPZ/Nf) nanocomposite at pH 2–10 were investigated at a glassy carbon electrode. Well defined reversible redox couples were observed in acidic solutions and irreversible in alkaline solutions. The (SNPs/CPZ/Nf) nanocomposite modified electrodes were characterized with a transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The apparent electron transfer rate constant (K_s), transfer coefficient (α) and the surface concentration (Γ_c) were determined by cyclic voltammetry and they were about 0.025 s^{-1} , 0.50 and $1.26 \times 10^{-6} \text{ mol cm}^{-2}$, respectively. Moreover, electrocatalytic oxidation of sulfide on the surface of modified electrode was investigated with cyclic voltammetry and amperometry methods at pH 7. The prepared modified electrode showed several advantages, such as a simple preparation method, high sensitivity, very low detection limits and excellent reproducibility. Moreover, the proposed sensor can be used for sulfide analysis in water samples.

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1. Introduction

The discovery of the antipsychotic agent chlorpromazine in the early 1950s and the advent of even more powerful phenothiazinic psychopharmacological agents represent a landmark in the history of the medical and psychiatric sciences [1]. Chlorpromazine hydrochloride is the most important compound in the large group of phenothiazine derivatives. It is widely used as a therapeutic agent for treating various mental and personality disorders, in the prevention of vomit spasms and as an intravenous anti-hypertensive. One of the common properties of phenothiazine and its derivatives is that they are easily oxidized and lose a single electron to become cation radicals [2–4] which are very active and can react with a number of substances [5–9]. It was found that cation radicals are colored and stable in acidic media. It has the ability for oxidation by many oxidizing agents with the formation of colored oxidation products. These cation radicals are easily formed by chemical [10–12], electrochemical [13,14], enzymatic [15] and photochemical [16] oxidation. The oxidation process involves two subsequent and distinct one-electron steps. The first is reversible

and results in the formation of a colored cation-radical. The second is irreversible and gives rise to the colorless sulfoxide [17]. One of the redox mediators that was used as a suitable homogeneous mediator in the electrooxidation of various compounds is chlorpromazine (CPZ) [18,19]. To our best knowledge, there are no reports concerning the use of CPZ in modification of electrodes for fabricated sensor.

Because of their unique electronic, optical and catalytic properties, nanoparticles have become the focus for scientific researchers [20,21]. The integration of nanoparticles and biomolecules into thin films is extremely significant, which has opened up a new route for the fabrication of chemical sensors and biosensors. As a non-metal oxide, silica (SiO_2) nanoparticles have extensive applications in chemical mechanical polishing and as additives to drugs, cosmetics, printer toners, varnishes and food. In recent years, the use of SiO_2 nanoparticles has been extended to biomedical and biotechnological fields, such as biosensors [22], biomarkers [23], cancer therapy [24], DNA delivery [25,26], drug delivery [27] and enzyme immobilization [28]. On the other hand, silica nanoparticles, because of their large surface area, good biocompatibility, and suitability for many surface immobilization mechanism, have been effectively used [29,30] and have proven to be excellent substrates in many fields ranging from biosensors to interfacial interaction studies [31]. Since the single silica material cannot transfer electron from analyte to electrode, as a result, organic–inorganic nanocomposite,

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such as the SiO₂ nanoparticles coupled with a redox mediator, have become attractive for many new electronic, optical or magnetic applications [32,33]. The resultant “nanocomposition” determines both the compatibility and the suitability of the probe towards the analyte, and thence assays are possible [34].

Sulfides (H₂S, HS⁻ and S²⁻) are found widely in natural water samples and wastewater and serve as a main pollution index for water [35]; also, it is used as a preservative in the food industry because its addition to several products (vegetables, fruits and several beverages) prevents oxidation, inhibits bacterial growth and assists in preserving vitamin C [36]. Due to potential toxicity of sulfide, the sulfide content more than the established threshold level should be strictly limited and must be adequately labeled. Therefore, the existence of methods allowing an accurate measurement of sulfide is very important. In aqueous solutions hydrogen sulfide is in equilibrium with bisulfide and sulfide ions. Total sulfide concentrations are usually reported as the sum of all three species. Many analytical methods for the sulfide assay have been reported, such as high performance liquid chromatography [37,38], capillary electrophoresis [39], chemiluminescence [40], and spectrophotometry [41]. Compared to electrochemical detections, these techniques are not convenient. For example, for the determination of traces of sulfide in solution, cathodic stripping voltammetry (CSV) can be a more suitable technique than the commonly used spectrophotometry from the viewpoints of detection limits and operational easiness [42].

Therefore, there is still an increasing demand in electrochemical detections, as these generally have the advantages of simplicity, short analysis time, low cost, high reproducibility, and sensitivity. A major problem arises due to the electrochemical oxidation of sulfide at bare electrodes, referred to as electrode fouling or poisoning, which decreases electrode reactivity and shortens its working life [43–46]. This problem can be overcome by construction of chemically modified electrodes (CME). The properties and electrochemical activities of CME that are constructed by the attachment of a catalytic species (organic or inorganic) to the surface of a base electrode, are found to be highly influenced by the nature of the adsorbed species and the electrode surface morphology [47–52]. Moreover, the sensing capability of these modified electrodes as environmental sensing tools for sulfide detection was another important area of application due to their high sensitivity, selectivity, simplicity and cheap construction [53–57].

A literature survey showed that there were not any reports on using CPZ as a mediator for construction of modified electrodes. We immobilized CPZ onto a GC electrode. However, the films were easily washed from the electrode with buffer solution and became unstable during the potential scan. SiO₂NPs/EtOH/water is attractive metrics for the incorporation of phenothiazine derivatives due to their excellent physical and chemical stability and the ease with which the silica gels can be prepared. The CPZ incorporated into SiO₂NPs/EtOH/water on the surfaces of GC electrode had well-defined electron transfer properties; however, the diffusion loss of CPZ into external solutions occurred. To overcome this problem, we immobilized CPZ into Nafion–silica composite films. When CPZ@SiO₂NPs were conjugated with a polymer Nafion (Nf) with favorable compatibility and film-forming ability, a promising platform for electrochemical analysis of CPZ and sulfide base on CPZ/SiO₂/Nf was further developed. The present research describes the electrochemical behavior of chlorpromazine as a modifier on the surface of electrode and an organic–inorganic nanocomposite material composed of silica nanoparticles, chlorpromazine and Nafion (SNPs/CPZ/Nf nanocomposite) was used for the construction of a new amperometric sensor for sulfide detection. The advantages of the sulfide amperometric detector based on the SNPs/CPZ/Nf nanocomposite GCE are as follows: a very low detection limit, high sensitivity inherent stability at pH 7, excellent catalytic activity

for sulfide oxidation and remarkable antifouling property toward sulfide and its oxidation product.

2. Experimental

2.1. Reagents

Chlorpromazine and sodium sulfide were purchased from Aldrich and Merck and used as received. Silica nanoparticles were procured from Sigma–Aldrich. Nafion (Nf) (v/v 5%) was obtained from Sigma chemical Co. A buffer solution (0.05 M) was prepared from di-sodium hydrogen phosphate (Na₂HPO₄), sodium dihydrogen phosphate (NaH₂PO₄), hydrogen chloride (HCl) and sodium hydroxide (NaOH) and was also purchased from Merck. Doubly distilled water was used to prepare all solutions. All electrochemical experiments were carried out at 25 ± 0.10 °C.

2.2. Apparatus

Electrochemical experiments were performed with a computer controlled μ -Autolab modular electrochemical system (Eco Chemie, Utrecht, The Netherlands) driven with GPES software (Eco Chemie). A conventional three-electrode cell consisting of a Ag/AgCl [KCl (sat)], Pt wire and (unmodified or modified) glassy carbon were used as reference, counter and working electrode, respectively. A personal computer was used for data storage and processing.

2.3. Preparation of the modified electrode

Prior to the modification, the bare GCE was polished successively with No. 1 to No. 6 emery papers and 0.5 μ m alumina slurry to mirror-like smoothness. Then, it was sonicated in ethanol and distilled water for 10 min to remove adsorbed particles. A 1.0% (v/v) Nafion solution was prepared by diluting the 5.0% (v/v) Nafion solution with ethanol. 1 mg silica nanoparticles and 1 mg CPZ were added to 5 mL 1.0% (v/v) Nafion solution, and then ultrasonicated for 30 min to form a homogeneous CPZ–SiO₂NPs–Nafion solution. Next, 5 μ L of the above solution was dripped onto cleaned GC electrode surface and dried at room temperature. Finally, the electrode was immersed in 0.05 M phosphate buffer solution (pH 7) and cycled in the potential range of 0.2–0.8 V using scan rate of 100 mV s⁻¹ for stabilization of the CPZ in the nanocomposite.

2.4. General analytical procedure

Cyclic voltammetric and amperometric techniques were used for sulfide detection. The cyclic voltammogram (CV) of 10 mL phosphate buffer solution with pH 7 was used for background correction. Then sulfide solution with different concentrations was added and their CVs were used for calibration curve construction. The CVs were recorded in the range of 0.3–0.85 V. The amperometric response of sulfide on SNPs/CPZ/Nf nanocomposite/GCE was obtained by addition of successive aliquots of 100 nM sulfide in phosphate buffer solution (pH 7) under the constant potential of 0.8 V.

3. Results and discussion

3.1. Morphological and electrochemical characterization of SNPs/CPZ/Nf/GC electrode

Fig. 1 shows the TEM images of SiO₂ nanoparticles (SNPs) and SNPs/CPZ/Nf nanocomposite film on the surface of glassy carbon electrode (GCE) revealing the attachment of nanocomposite film

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