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A novel and improved surfactant-modified Prussian Blue electrode for amperometric detection of free chlorine in water

Pedro Salazar[a,b,*], Miriam Martín[b], Francisco J. García-García[a], José Luis González-Mora[b], Agustín R. González-Elipe[a]

[a] Laboratory of Nanotechnology on Surfaces, Institute of Materials Science of Seville (CSIC-Univ. Sevilla), Calle Américo Vespucio 49, 41092 Sevilla, Spain
[b] Neurochemistry and Neuroimaging Group (Laboratory of Sensors, Biosensors and Materials), Faculty of Medical Sciences, University of La Laguna, Campus de Ofra s/n, 38071 La Laguna, Tenerife, Spain

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ABSTRACT

A surfactant-modified Prussian Blue (PB) electrochemical sensor has been developed. Benzethonium was used to assist the electrodeposition of PB onto a glassy carbon electrode (GCE). The surface coverage ($\Gamma^{0}_{Fe^{3+}}$) was 7.75×10^{-8} mol cm^{-2}, five times higher than the value obtained in the absence of surfactant, and the film thickness of ca. 123 nm. SEM, EDX, Raman were used to characterize the electrodes while their electrochemical analysis proved a superior performance for the surfactant modified PB film. Cyclic voltammetry and amperometry were used to study the sensor ability to detect chlorine, and the main experimental variables were optimized. Under optimized conditions, the sensor presented a sensitivity of 12 μA ppm^{-1} cm^{-2}, a linear range from 9 ppb to 10 ppm and a reproducibility of 4.2%. For the first time, we proved the sensor performance for real applications. Thus, chlorine was determined in tap water and the obtained concentrations validated with a standard colorimetric method. The obtained results showed that our sensor is highly performant and reliable for applications involving determinations of environmental residual chlorine.

1. Introduction

During the last century control of the quality of drinking water has attracted a lot of resources and the attention of scientists, authorities and consumers. Waterborne diseases such as typhoid fever, cholera and Hepatitis A or E cause the illness or death of many people, mainly among fragile groups such as young children, elders and people with a weakened immune system. Other microorganisms such as *E. coli*, Salmonella, Calicivirus, although inducing less dangerous diseases characterized by diarrhoea as main symptom, also constitute a serious health problem [1–5].

The first WHO (*World Health Organization*) document dealing specifically with public drinking-water quality was published in 1958 as International Standards for Drinking-Water, being subsequently revised during last decades. In 1998 the European Union accepted the Drinking Water Directive 98/83/EC. At present these guidelines define a reference framework of the quality conditions for European drinking water.

To obtain safe drinking water, most part of pathogenic microorganisms must be removed by means of water treatment techniques, such as coagulation [6], flocculation [7], settling [8] and filtration [9]. The most frequently used method of disinfection is chlorination, although ozonation [10], UV irradiation [11], chloramination [12] and application of chlorine dioxides [13] are also used. In general, an efficient safety disinfection of drinking water is achieved by applying a final treatment with chlorine as final purification step. Its easy production at relatively low costs is a clear competitive advantage of chlorine with respect to the other methods.

Residual disinfection with chlorine is also applied to provide a safeguard against low-level contamination and pathogen growth within the distribution system. This defines a clear need for chlorine monitoring and control during water treatment and distribution cycles [14,15]. In general, determination of free chlorine concentration, taken as the sum of dissolved chlorine gas (Cl_2), hypochlorous acid (HClO) and hypochlorite anion (ClO^-), is of great importance to define quality levels of disinfection in tap, drinking and swimming pool waters [16].

Spectrophotometric monitoring of N,N-diethyl-p-phenylendiamine (DPD) [17,18] is likely the most common

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[*] Corresponding author at: Laboratory of Nanotechnology on Surfaces, Institute of Materials Science of Seville (CSIC-Univ. Sevilla), Calle Américo Vespucio 49, 41092 Sevilla, Spain. Tel.: +34 954489527.
E-mail addresses: psalazar@ull.edu.es, psalazar@icmse.csic.es (P. Salazar).

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determination method of free and total chlorine in water and wastewater (Standard Methods 4500-Cl G and ISO 7393/2). This procedure is simple but cannot be applied in continuous systems. By contrast, electroanalytical methods are more straightforward due to their simplicity, potential high sensitivity and selectivity, low cost, real-time output and the possibility to develop user-friendly and wireless integrated devices suitable for on-line monitoring. The need of robust electrochemical transducers for this application has prompted the development of various electrochemical chlorine sensors using different electrode materials (gold, platinum, glassy carbon, carbon nanotube-modified transducer, etc.) [19,20] and electrochemical techniques [13,21–25].

Prussian Blue (PB), $Fe_4[Fe(CN)_6]_3$, belongs to a transition metal hexacyanometallate family that was firstly utilized as a blue pigment already in the 1700s. Electrochemical properties of PB were investigated by Neff as early as 1978 [26]. Then, Itaya et al. [27] showed that the reduced form of PB (Prussian White, PW) displayed catalytic activity for the reduction of H_2O_2. More recently, in 1994, Karyakin et al. [28], showed that PB may act as artificial peroxidase and demonstrated that it can be an excellent material for the fabrication of biosensors. This pioneering work opened the way for new developments in this application as evidenced by a vast bibliography on the subject [29]. New applications for PB and its analogues have been developed including the determination of new molecules such as vitamin B-6, thiocholine and other thiols, dopamine, norepinephrine, epinephrine, morphine, cysteine, methionine, ascorbic acid, or isoprenaline [30]. Determination of free chlorine with this system was also intended by Shim et al. [31], using a carbon nanotube/Prussian Blue paste electrode used as amperometric sensor. However, last work only showed partial results without a deep analysis and discussion. In this context, we showed recently that the addition of a cationic surfactant such as BZTC (benzethonium chloride) during the electro-deposition of PB significantly improves its electrocatalytic and electrochemical properties and increase its stability in neutral and basic media [32,33].

In the present work we develop a BZTC-modified PB electrode for the quantitative determination of free chlorine in water. The system consists of glassy carbon electrodes (GCEs) functionalized with BZTC-modified PB films, GCE/PB(BZTC). The beneficial effects of using BZTC during PB electrodeposition are discussed. In addition, the effect of main experimental variables such as pH, detection potential are systematically carried out to define the range of working conditions of the device transducer. For the first time the analytical parameters of this new transducer electrode are evaluated with real tap water samples and compared against a standard colorimetric method of free chlorine determination.

2. Experimental

2.1. Reagents and solutions

Sodium hypochlorite (4.00–4.99%) and other chemicals were obtained from Sigma and used as supplied. Stock solutions were prepared in doubly distilled water (18.2 MΩ cm, Millipore-Q), and stored at 4 °C when not in use. The stock chlorine solution (100 ppm) was prepared in water just before using.

2.2. Instrumentation

Glassy carbon electrodes (GCEs, 3 mm diameter) were purchased from CH Instruments Inc., USA. Electrochemical measurements were performed with a DRP-STAT400 potentiostat and data were acquired with Dropview software (DropSens). For all electrochemical measurements, an Ag/AgCl (3 M KCl) and a Pt wire were used as reference and counter electrodes, respectively. Field emission scanning electron micrographs (FE-SEMs) and energy dispersive X-ray spectra (EDX) were obtained using a HITACHI S 4800 microscope. Raman and absorbance spectra were taken with a HORIBA HR-800-UV microscope and a VARIAN Cary-100-UV/Vis spectrophotometer respectively.

2.3. PB electrodeposition

The background electrolyte solution consisted of (0.02 M HCl and 0.1 M KCl; pH 1.7). Electrodeposition of the BZTC-modified PB composite film onto GCE was accomplished by introducing the electrode in the background solution with 1.5 mM $FeCl_3$, 1.5 mM $K_3[Fe(CN)_6]$ and 2 mM benzethonium chloride (BZTC) [32], this latter added just before the electrodeposition. Then, GCEs were cycled between −0.2 and 1.0 V at a scan rate of 0.1 V s^{-1} (20 cycles). Unmodified PB films were prepared under the same conditions except for that the solution was surfactant free.

2.4. Electrochemical characterization

Electrochemical characterization was done in a background electrolyte solution using cyclic voltammetry (CV) at 0.01 V s^{-1}. Constant Potential Amperometry (CPA) was employed to study the sensitivity against chlorine using different configurations and different experimental conditions.

2.5. Chlorine sensor calibrations

Free chlorine sensitivities were obtained by using the following protocol. Firstly, sensors were placed in 25 mL of a stirred 0.1 M phosphate buffer solution (pH 5.5) with 0.1 M KCl. Unless otherwise stated, the applied potential for the amperometric experiments was −0.1 V versus the Ag/AgCl (3 M KCl) reference electrode. After stabilization of current (~200 s), chlorine aliquots were added and the electrode response measured after each addition. All experiments were performed at room temperature. Finally, free chlorine concentrations determined in real samples were compared with those obtained using a standard DPD colorimetric method.

3. Results and discussions

Fig. 1a and b shows the CVs recorded for 20 cycles during film formation for PB and surfactant-modified PB films, respectively. The progressive increase of the area of the CV curves in successive cycles supports an enhancement of the accumulated charge and confirms the correct deposition of PB onto the GCE surface. From the comparison of the two sets of curves it is also apparent that, in comparison with the unmodified film, just from the first cycle the CV response was higher during the formation of the BZTC-modified PB film. In addition, both the charge accumulated in the anodic (Q_{ox}) and cathodic (Q_{rd}) peaks and the deposition rate, expressed as charge accumulated per cycle under the anodic (forward) peak, were higher in the presence of BZTC. This confirmed the beneficial effect of this compound during electrodeposition of PB [32,33]. In this way, electrodeposited PB films are characterized by a linear increase in accumulated charge during the first cycles followed by a plateau that indicates a saturation for the deposition of this compound on the electrode surface. In contrast, for the BZTC-modified PB films the accumulated charge continued increasing in successive cycles during the entire deposition time. This behaviour clearly proves a higher deposition efficiency and the accumulation of a higher amount of PB onto the GCE surface. The beneficial effect of BZTC during electro-deposition may be understood according to