Preparation of a 2-(4-fluorophenyl)indole-modified xerogel and its use for the fabrication of screen-printed electrodes for the electrocatalytic determination of sulfide

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Abstract

The preparation of a 2-(4-fluorophenyl)indole-modified xerogel (FPIX), pure or further modified with platinum (Pt-FPIX) and their use for the fabrication of screen-printed electrodes for the electrocatalytic determination of sulfide in synthetic and real samples is described. Synthesis protocol and some preliminary identification studies of 2-(4-fluorophenyl)indole-modified xerogel are given. The fabrication of FPIX screen-printed electrodes (SPEs) and the preparation of FPIX and Pt-FPIX chemically modified graphite electrodes (CMEs) by using a mixture of FPIX/graphite-based polymer thick film ink are also described. The electrocatalytic behavior of the FPIX- or Pt-FPIX-CMEs to sulfide was tested with cyclic voltammetry (CV). The optimization of various working parameters such as xerogel loading, working pH, utilization of a cellulose acetate outer protective membrane, as well as the interference effect of various reducing compounds was also tested with CV or amperometric measurements in both, batch and flow conditions. Discrimination between the electrocatalytic effect of FPIX on the sulfide oxidation and the increase of the film conductivity being induced from the incorporation of platinum in the xerogel, regarding their contribution to the overall measuring signal was attempted by impedance spectroscopy. FPIX-SPEs, poised at +450 mV versus Ag/AgCl, at pH 5.5 were utilized for the determination of sulfide in synthetic and real samples. The proposed method correlates well with a colorimetric method. Calibration graphs were linear over the range 0.01–2.0 mM sodium sulfide and the RSD was 2.2% (0.25 mM sodium sulfide, $n = 12$). Recovery ranged from 93 to 105%. FPIX-SPEs showed both very good working and storage stability. They retain almost 95% of their initial activity after 50–60 runs and can be stored at room temperature with no remarkable loss of their activity for more than 1 month.
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1. Introduction

Sulfide is formed in wastewater by the action of anaerobic bacteria on organic matter. Sulfide salts are used in industrial waste streams in order to control the levels of several toxic metals (e.g. mercury, lead) discharged into the environment, since many metal sulfides are insoluble and precipitate out in the waste stream [1]. There are limits on the total level of sulfide permitted in waste discharges because of its toxicity, capacity to remove dissolved oxygen and its capability to produce hydrogen sulfide. Obviously, the level of sulfide in industrial and urban waste has a tremendous impact on public acceptance and safety as well as on the longevity of concrete infrastructure [2]. Recently, sulfide electrocatalysis has attracted enormous scientific attention, and is the objective of much current research on the design of fuel cells for harvesting energy from marine sediments [3].

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A number of standard methods are available for the determination of sulfide. Most popular and well known is the colorimetric method of methylene blue [4]. Other methods such as spectrophotometry [5], fluorometry [6], potentiometry [7], molecular absorption spectroscopy [8], liquid chromatography [9] and coulometry [10] have been reported.

Amperometric methods based on mediated oxidation sulfide through 2,6-dichlorophenolindophenol [11], cobalt phthalocyanide [12] or hexadecylpyridinium-bis(chloranilato)-antimonyl(V) [13] have also been reported. Other approaches include electrodeposition of palladium onto glassy carbon electrodes [14] and nickel electrodes in alkaline media [15]. A comprehensive review by Lawrence et al. [16] describes also in detail the basis of many of the current approaches to sulfide detection.

Sol–gel-derived glasses have emerged as a new class of materials well suited to the immobilization of mediators or biomolecules. Such attempts include sol–gel ceramic film incorporating methylene blue [17], a meldola's blue functionalized inorganic–organic hybrid material [18], a ferrocene-modified glucose oxidase electrode [19], a glucose oxidase Au-doped siloxane electrode [20], an enzyme–graphite–xerogel electrode with ferricyanide as a mediator [21], a Co(II) phthalocyanine-modified silica on carbon paste electrodes [22], a tetrathiafulvalene-modified electrode in conjuction with silica film [23], a sol–gel enzyme layer onto a Nafion–methylene green-modified electrode [24] and a sol–gel-derived glass combined with an Eastman AQ 55D polymer and thionine [25] as a mediator.

In general, sol–gel-based materials with certain tailormade properties, i.e., efficient electrocatalysis of various electroactive compounds, fouling protection, exclusion of interferants, are of great importance for the development of (bio)chemical sensors.

We first proposed here the preparation of the 2-(4-fluorophenyl)indole-modified xerogel based on the pioneering work of Spange et al. [26]. A number of other fluoro compounds, including 4-fluoro-4-hydroxy-benzophenone, 5-fluorouracil, 6-fluoro-4-chromanone, 2-fluoro-9-fluorenone, 4-fluoroaniline, tetrafluro-1,4-benzoquinone, 3-fluoro-2-hydroxybenzaldehyde, 5-fluoroindole and 6-fluoro-4-hydroxycoumarin were also tested in the specific synthetic route for the preparation of organically modified xerogels. The present work explores the use of a novel xerogel for the preparation of CMEs or the fabrication SPEs that were successfully tried in the development of highly selective amperometric sensors for the determination of sulfide.

The proposed sensor shows similar [11-13,16] or lower [14] sensitivity compared with other proposed amperometric sulfide sensors. The simplicity and the low cost of its construction are certain advantages compared with sulfide sensors based on nickel hydroxide [16] or palladium particles [14]. Moreover, it is highly selective towards sulfide, allowing thus its direct use to real samples, without any prior chromatographic separation [14]. Other proposed methods have not challenged in real samples [12,16].

2. Experimental

2.1. Reagents

2-(4-Fluorophenyl)indole (FPI, $C_{14}H_{10}FN$, MW 211.23, m.p. 190–192 °C) was purchased from Apollo Scientific Ltd. (Cheshire, UK). 3-Aminopropyltriethoxysilane (APTES), tetraethoxysilane (TEOS) and *N,N*-dimethyloctylamine were obtained from Merck (Darmstadt, Germany) and used without further purification. Sodium sulfide and ethyl cellulose was purchased from Sigma (St. Louis, USA). 2-(2-Ethoxyethoxy)ethyl acetate (2-BEA) was purchased from Fluka (Deisenhofen, Germany). Silver (PF410) and graphite (421SS) inks were purchased from Acheson Colloiden, B.V. (Scheemda, The Netherlands). A nail hardener (Revlon, New York) was used as an insulating ink. PVC matrix (Genotherm, 0.4 mm thickness) was obtained from Sericol Ltd. (London, UK). Screens were constructed by DEK Printing Machines Ltd. (Dorset, UK), with 250 mesh/in. stainless steel.

The stock sulfide solution (about 0.5 M) was prepared by dissolving $Na_2S\cdot9H_2O$ crystals in degassed distilled water and kept at +4 °C, stable for a maximum of 2 weeks. This solution was periodically standardized with the methylene blue colorimetric method. Working standard solutions were prepared before use in degassed distilled water.

2.2. Apparatus

Screen-printed electrodes were fabricated using a Model 247 screen printer (DEK). All electrochemical experiments were conducted with a computer-controlled potentiostat, PGSTAT12/FRA2 (ECO CHEMIE, Utrecht, The Netherlands). Cyclic voltammetry, amperometry and capacitance experiments were performed with a voltammetry cell (VC2, BAS, USA) using graphite electrode (RW0001, 6.5 mm i.d., Ringsdorf-Werke, Germany) or with a 20 ml thermostated conical cell using SPE as the working electrode, a Ag/AgCl/3 M KCl (BAS) as reference electrode and a Pt wire as auxiliary electrode. All experiments were carried out at room temperature.

A Shimadzu UV2100 spectrophotometer was used for performing the reference method based on methylene blue formation in acidic medium [4].

2.3. Procedure

(10.0–x) milliliters of 0.25 M phosphate buffer in 50 mM KCl, pH 4.5–8.5 were introduced in the reaction cell and stirred at a moderate speed with a magnetic stirrer. When a stable current value was reached, appropriate values (x) ml of sodium sulfide were added and current changes due to the sulfide oxidation at 450 mV were recorded. The steady-state current response was taken as a measure of the analyte concentration.

2.4. Preparation of the modified electrodes

Before use, spectroscopic graphite rods were treated according to a previously described procedure [13]. Fifty milligrams of the tested xerogels (FPIX or Pt-FPIX) was mixed with 1 ml of the carbon-based ink (diluted 1 + 1 with 2-(2-ethoxyethoxy)ethyl acetate) and left to homogenize under stirring overnight. The surface modification was made by dipping the graphite rods in the mixture and allowed to evaporate at ambient temperature overnight, following thorough washing with distilled water.

Screen-printed electrodes were fabricated according to a previously described method [13]. Working electrodes were modified by applying 20 μl of the FPIX or Pt-FPIX-modified carbon-based ink over a graphite-based resin overlay pad [13]. Electrodes were left to dry at ambient temperature overnight, and then 10 μl of a 2% cellulose acetate solution was pipetted over the sensing layer. Electrodes were left again to dry at ambient temperature overnight.

For impedance spectroscopy experiments, platinum electrodes were covered with 10 μl of a mixture of 50 mg FPIX or Pt-FPIX in a 2% cellulose acetate solution and allowed to dry overnight.

2.5. Sample preparation

Samples were collected from the sewage treatment plant of the city of Ioannina. Synthetic samples came from the main stream after spiking known amounts of sodium sulfide. Samples indicated as "anaerobic" are coming from the anaerobic section of the plant. *Safety note*: Sodium sulfide and anaerobic samples must be handled with extreme caution! Samples were diluted by a factor of 50 and 500 with degassed buffer solution, respectively. Samples were filtered through a Whatman paper No. 41 in order to remove solid (sludge) waste and were analyzed without further pretreatment.

2.6. Preparation of the 2-(4-fluorophenyl)indole-modified xerogel

The reaction pathway for the preparation of the 2-(4-fluorophenyl)indole-modified xerogel is depicted in Scheme 1. 0.276 g (1.31 mmol) of 2-(4-fluorophenyl)indole was dissolved in 2.94 ml (1.31 mmol) TEOS with stirring. 0.23 ml (1.31 mmol) APTES and 0.275 ml (1.31 mmol) *N,N*-dimethyloctylamine were then added. The mixture was heated to reflux for 24 h at 166 °C. A dark-yellow coloration was developed and a nonviscous solution was formed. After cooling to room temperature, the solution was treated with 7.5 ml of ethanol and 2 ml of distilled water and the gel formation began after about 30 min. The solid gel was dried at room temperature in vacuo and then the unreacted fluoro compound was removed by Soxhlet extraction with acetone. The xerogel was re-dried in vacuo. For the preparation of the Pt-FPIX, the same procedure, in the presence of 10 mg platinum powder and for a reflux period of 72 h, was followed.
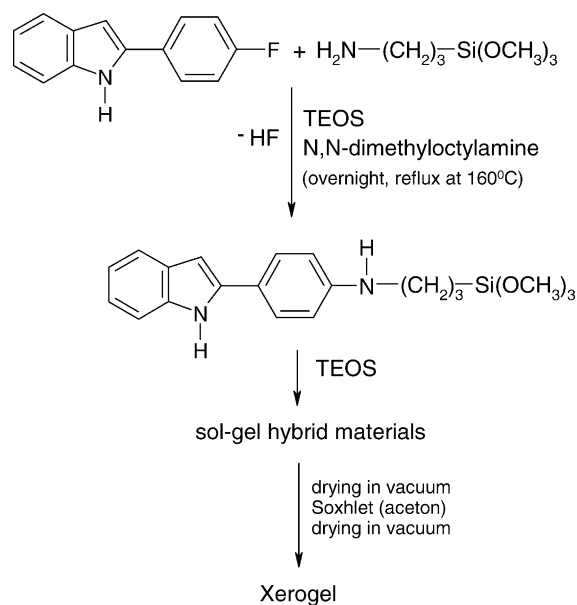
Scheme 1. Preparation route of 2-(4-fluorophenyl)indole-modified xerogel.

2.7. Preliminary characterization studies

The synthesis of xerogel includes the nucleophilic substitution of a fluorine atom of 2-(4-fluorophenyl)indole, by 3-aminopropyltrimethoxysilane that is bonded by an alkyl chain to a trialkoxysilane group. The IR-Reflectance Spectroscopy (Perkin Elmer Corp., USA) spectra gave the following peaks:

2-(4-Fluorophenyl)indole: ν = 3416 [ν(NH$_{indole}$)], 3051, 2926, [ν(CH)], 1603 [δ(NH$_{indole}$)], 1232 [ν(C−F)]; *FPIX*: ν = 3437br [ν(Si−OH)], 2983, 2929 [ν(CH$_2$)], 1639 [δ(NH$_{indole}$)], 1594sh [δ(NH$_{iminic}$)], 1458 [δ(CH$_2$)], 1075 [ν_{as}(Si−O−Si)], 796 [ν_{sym}(Si−O−Si)], 455 ρ[(Si−O−Si)])]; and Pt-*FPIX*: ν = 3435br [ν(Si−OH)], 2929 [ν(CH$_2$)], 1638 [δ(NH$_{indole}$)], 1560 [δ(NH$_{iminic}$)], 1460 [δ(CH$_2$)], 1076 [ν_{as}(Si−O−Si)], 795 [ν_{sym}(Si−O−Si)], 456 ρ[(Si−O−Si)].

The very broad and intense band at 3437 cm^{-1} of FPIX is attributed to the silanol groups. In xerogels this band is very broad and intense, and is attributed to stretching modes of hydrogen-bonded silanols [27]. The very strong band at 1075 cm^{-1}, the weak at 796 cm^{-1} and the broad band at 456 cm^{-1} are attributed to ν_{as}, ν_{sym} and rocking modes of the siloxane bridges [(Si−O−Si)] of the silicate matrix. The very intense band at 1232 cm^{-1} of the stretching mode [ν(C−F)] is disappeared in the xerogel, while the stretching and bending mode of the NH$_{indole}$ group is retained in xerogel [27,28]. In the mid-infrared region, the FPIX and the Pt-FPIX exhibit the same profile, while in the far-infrared region there are pronounced differences. A new band for Pt-FPIX at 233 cm^{-1} may be assigned to Pt−O bond [29,30]. It is not discernible, from the infrared spectra, which the platinum causes a covalent modification to the xerogel or it is encapsulated in the

silicate matrix. In that case, the encapsulated platinum atoms are physically bound.

3. Results and discussion

3.1. Electrocatalytic oxidation of sulfide

A series of organically modified xerogels-CMEs (50 mg xerogel/1 ml ink) were produced and their efficiency towards the electrocatalysis of various analytes, i.e. NADH, sulfide, phenol, cysteine, glutathione, was tested with cyclic voltammetry experiments in 50 mM phosphate pH 6.5 in 50 mM KCl composite electrolyte, at a scan rate of $0.1\,V\,s^{-1}$. Under these conditions, FPIX-CMEs gave an almost flat cyclic voltammogram with a pair of weak peaks at $-0.1\,V$ (data not shown). In contrast with the conventional CMEs (formation of a mediator monolayer that obeys a Langmuir-type isotherm over a smooth graphite surface) where the absorbed mediator exhibit a clear electrochemistry [11,13], polymer based (sol–gel, screen-printed electrodes, polymeric membranes) electrodes fair to present well-defined redox peaks [13,17,31]. The nature of the immobilized mediator (high concentration, entrapment in the polymeric film) as well as electrochemical reactions of adjacent silicon-bridged mediator moieties result to an extended broadening of the redox waves. Study of the electrochemical behavior of the electrode in $CH_2Cl_2/[Bu_4N][PF_6]$ instead of aqueous solutions has been proposed [31].

As can be seen in Fig. 1, FPIX-CMEs, upon the addition of 5 mM sulfide, give rise to a large catalytic current, even at low potentials of 0–0.2 V, due to the mediated oxidation of sulfide by the FPIX. It is obvious that in the presence of the xerogel, an important lowering of the overpotential of at least 200 mV was achieved. The sulfide oxidation on the plain electrode (scan a) appears at a high overpotential >0.55 V in agree-

Fig. 2. Cyclic voltammograms of an FPRIX-CME (50 mg xerogel/ml ink) in 50 mM phosphate in 50 mM KCl, pH 5.5 for various concentrations of sodium sulfide: (a) buffer, (c) 2.5 mM, (d) 5 mM, (e) 10 mM. Scan (b) illustrating the CV of a blank electrode in the presence of 2.5 mM sodium sulfide. Scan rate, $0.1\,V\,s^{-1}$.

ment with earlier reports [11,13]. In contrast to sulfide, low catalytic currents were recorded upon the addition of 5 mM of NADH, phenol, cysteine and glutathione, thus showing the high selectivity of the proposed catalyst towards sulfide.

Fig. 2 shows cyclic voltammograms obtained with a resin-CME, scan b (used as blank) and a FPIX-CME, scan c, for a 2.5 mM sodium sulfide in 50 mM phosphate buffer solution pH 5.5 in 50 mMKCl. Comparing scans (b) and (c), it is obvious that the electrocatalysis of sulfide is totally attributed to the presence of FPIX. Under the same experimental conditions, using the FPIX-CME, the dependence of the concentration of sulfide to the catalytic current was also investigated in the presence of 5 mM sulfide, scan d, and 10 mM sulfide, scan e. The anodic current increases proportionally to the concentration of sulfide. Plots of the catalytic peak current are linearly increased with the square root of the sweep rate (data not shown) suggesting that at sufficient overpotential the reaction is diffusion-controlled [32,33].

Xerogel loading test was carried out for three different mixtures of the xerogel (25, 50 and 75 mg/ml ink). Best results in terms of sensitivity were obtained with the most concentrated mixture; however, the reproducibility of the resulting films was poor due to appearance of crackings on the film surface. Subsequent experiments were carried out using a mixture of 50 mg xerogel/ml of carbon-based ink.

In the literature, there is no any relevant work to support the electrocatalytic effect of the proposed modifier on sulfide. A strong evidence for supporting our claim is of course, the large anodic catalytic current shown in Fig. 1. Moreover, a simple wet chemistry test, i.e., addition of 5 mM sulfide in (a) 10 ml working buffer (blank), (b) 0.1 g FPIX/10 ml working buffer and (c) 0.1 g FPI/10 ml working buffer gave extra evidence that sulfide ions are being oxidized, since only in (b), supernatant solution was colored yellow. This chromatic change can be attributed to the formation of sulfur.
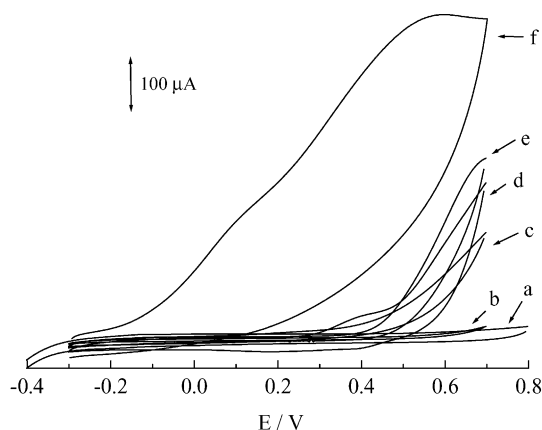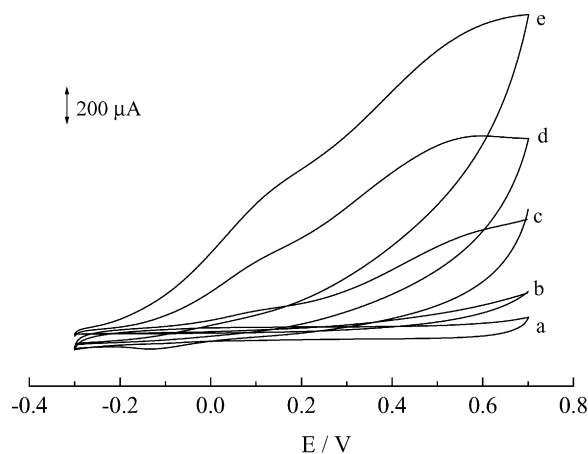

Fig. 1. Cyclic voltammograms of an FPRIX-CME (50 mg xerogel/ml ink) in 50 mM phosphate in 50 mM KCl, pH 6.5 for various reducing compounds: (a) blank, (b) glutathione, (c) cysteine, (d) phenol, (e) NADH and (f) sodium sulfide. Concentration, 5 mM. Scan rate, $0.1\,V\,s^{-1}$.
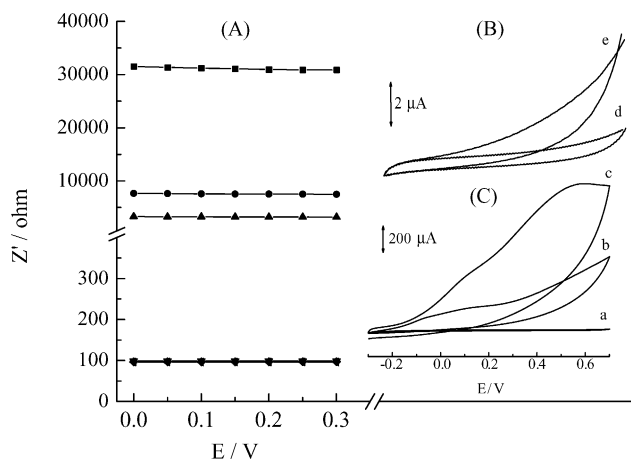
Fig. 3. (A) Measurement of the real impedance (Z') at 100 Hz and 10 mV amplitude, with respect to the potential for (first break) FPIX-, Pt-FPIX-CMEs (50 mg xerogel/ml ink) and blank electrode and (second break) (●) FPIX-, (▲) Pt-FPIX-cellulose acetate (50 mg xerogel/ml 2% cellulose acetate)-modified platinum electrodes and (■) blank electrode. (B) CVs for a (d) FPIX-CA platinum electrode, (e) Pt-FPIX-CA platinum electrode in the presence of 5 mM sodium sulfide in 50 mM phosphate in 50 mM KCl, pH 5.5. (C) CVs for a (a) blank graphite electrode, (b) Pt-FPIX-CME and (c) FPIX-CME in the presence of 5 mM sodium sulfide in 50 mM phosphate in 50 mM KCl, pH 5.5. Scan rate, 0.1 V s^{-1}.

Mechanistic details are not provided, since the experimental data so far cannot safely support a mechanism.

3.2. pH profile

In this point it is useful to make clear that the term "sulfide" is improper. According to the distribution diagram of sulfides [34], sulfide ions are dominated for pH > 12 whereas within the pH region tested in the present study, dissolved hydrogen sulfide is the predominant form for pH < 5.5, for pH > 7 hydrosulfide is the major form whereas at pH 7, an equal molar mixture of H_2S and HS^- forms exists. The effect of pH on the performance of the system was tested in a 50 mM phosphate buffer in 50 mM KCl, within the pH range 4.5–8.5 (data not shown). Best results, in terms of sensor sensitivity, were obtained at pH 5.5.

3.3. Discrimination between electrocatalytic efficiency and film conductivity

As mentioned above, in order to increase the conductivity of the sol–gel- or xerogel-based films, doping with various metals such as gold, palladium, iridium and platinum has been proposed [19,20,35]. Based on these results, we proceed to the preparation of the Pt-modified FPIX.

A comparative test between FPIX- and Pt-FPIX-CMEs was carried out by performing CV and as can be seen in Fig. 3C, FPIX-CMEs showed considerable higher electrocatalytic waves. Due to the higher conductivity of Pt-FPIX, a higher catalytic wave was expected. In order to distinguish between the conductivity and the electrocatalytic ability of

each membrane, various diagnostic experiments were performed. Confusion is often noted in the literature since these terms are treated or meant as the same. This is because the overall behavior of a sensor, i.e., a measurable catalytic current, is the result of the above-mentioned parameters.

The conductivity of the various films was measured with impedance spectroscopy. Fig. 3A shows plots of impedance (real) against potential from 0 to 0.3 V (each point represents a potential step of 50 mV) at a 50 mM phosphate buffer pH 5.5 in 50 mM KCl versus a Ag/AgCl/3 M KCl reference electrode. At this potential window (see Fig. 1), there is no faradaic reaction, so the film-covered electrodes can be represented by an RC circuit consisting of the film resistance and double-layer capacitance. Moreover, all the experiments were carried out at a 30 kHz frequency (the voltage amplitude of the sine waveform is 10 mV), in order to drastically suppress the contribution of the capacitance to the overall impedance and to ensure thus that the recorded impedance is largely attributed to the film resistance. As can be seen from Fig. 3A, the resistance of the film is not the limiting parameter in the electrochemical performance of the FIPX- or Pt-FPIX-carbon-based ink films, since the carbon-based ink is highly conductive. Both films as well as a non-xerogel-modified film exhibit similar conductivities (93–99 Ω). In this case, as it can be seen from Fig. 3C, FPIX-CME is more effective than Pt-FPIX-CME, with respect to sulfide electrocatalysis, meaning thus that the incorporation of platinum in the silica matrix inhibits or destroys the catalytic properties of the indolphenol moieties.

On the other hand, if the conductivity being the limiting factor in the electrochemical performance of the films (this can be achieved by replacing the highly conductive carbon ink with the non-conductive cellulose acetate; relative conductivities of the pure cellulose acetate, Pt-FPIX-CA and FPIX-CA films are 31,100, 9100 and 3000 Ω), then a higher catalytic current is recorded for the Pt-FPIX film as shown at CVgrams in Fig. 3B.

3.4. Interferences

FPIX-SPEs showed a remarkable selectivity towards sulfide. Their response in the presence of a big variety of reducing compounds was almost not detectable. As it can be seen from the CVs in Fig. 2, the proposed modifier is quite selective to sulfide. Moreover, the use of cellulose acetate membrane offers permselectivity based on size exclusion with an MW cut off of 100 Da [13]. Interference from various reducing species was investigated by applying the method of mixed solutions in the presence of 0.2 mM sodium sulfide. The relative responses for a 10-fold higher concentration of uric acid, homocysteine, paracetamol, ascorbic acid, thiamine, riboflavin, penicillamine, sulfite, sodium dithionite, parathion, malathion, pesticides Methomyl^{TM} and Lannate^{TM} were ranged from 100 to 108% compared to the response shown with pure solution of 0.2 mM sulfide taken as 100%.
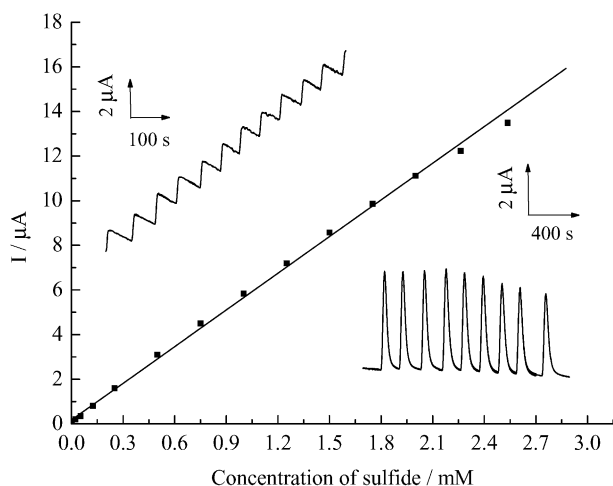
Fig. 4. Calibration curve for FPIX-SPEs in 50 mM phosphate in 50 mM KCl, pH 5.5 at 0.45 V. Up-left image: repeatability of the results for 0.25 mM sodium sulfide using FPIX-printed electrode at the same conditions. Down-right image: FIAgrams for successive injections of 0.25 mM sodium sulfide using FPIX-CME at the same conditions. Sample size, 120 μl. Flow rate, 0.5 ml min^{-1}.

3.5. Analytical performance

Despite their efficiency in promoting the electrocatalysis of sulfide, FPIX-CMEs were not used further in analytical applications, as their stability in flow conditions did not meet the standards of CMEs. FPIX-CMEs were mounted in a three-electrode wall-jet type flow cell and their reproducibility was evaluated by successive injections of 0.25 mM sodium sulfide. As can be seen in Fig. 4 (down-right inset graph), the peak height of the obtained FIAgrams is gradually decreased. Reasons coupled with the mechanical strain of the film due to the low adhesion of the film onto the graphite rod or with the improper hydrodynamic characteristics of the film are more likely, since leaching or deactivation of the modifier from so earlier injections is less likely.

In order to overcome this problem, screen-printed electrodes were fabricated. FPIX-SPEs maintained the good characteristics of CMEs in terms of coupling efficiency (electrocatalysis) of sulfide. Moreover, they showed good working and storage stability. Furthermore, this type of sensor is very cheap and easy to produce in great numbers, thus making it ideal for single use. The latter feature is of great interest for environmental applications, especially in the case of toxic samples.

As can be seen in Fig. 4 (up-left inset graph), the relative standard deviation for a standard solution of 0.25 mM sodium sulfide was calculated 2.2% RSD ($n = 12$).

The reproducibility of fabrication was checked applying amperometry, on a 0.1 mM solution of sodium sulfide with 10 randomly chosen electrodes and found to be 4.2%. This reproducibility is satisfactory and can be further improved using screens of higher mesh, as this parameter is responsible for the texture and the size of the printed (working) area.

Table 1
Determination and recovery studies of sulfide in waste water samples

Sample	Proposed method[a] ($\times 10^{-4}$ M)	Reference method ($\times 10^{-4}$ M)	Relative error (%)	Recovery[b] (%)
Synthetic 1	2.56 ± 0.03	2.65	−3.4	93
Synthetic 2	2.61 ± 0.03	2.46	+6.1	102
Synthetic 2	1.17 ± 0.02	1.12	+4.5	105
Anaerobic	7.60 ± 0.05	7.01	+7.1	105

[a] Average of three runs ± S.D.
[b] Addition of 0.15 mM sodium sulfide.

The reproducibility of fabrication is also a matter of printer quality; however, the used printer offers high reproducibility of the applied pressure and speed of the squeegee.

Good linearity, 0.01–2.0 mM sulfide, for the FPIX-SPEs ($r = 0.999$) was achieved. For a signal-to-noise ratio of 3, the detection limit of the method was calculated 6 μM.

The proposed method was applied to wastewater samples for the determination of sulfide. The results of various samples are summarized in Table 1. The results were compared with those obtained with a spectrophotometric reference method [4]. The accuracy of the method was also verified by recovery studies adding standard sodium sulfide solutions to samples. Recoveries of 93–105% were achieved, as shown in Table 1.

3.6. Stability of the sensor

Screen-printed electrodes explore a satisfactory working and storage stability. The working stability of the sensors was studied by continuous exposure to the working buffer, measuring the produced current after the injection of a 0.2 mM solution of sodium sulfide. As a result the final activity (current response versus initial current response × 100%) was 95% after 50–60 injections. FPIX-SPEs also displayed good storage stability if stored dry at room temperature, when not in use. They retained their initial activity for almost 1 month.

Acknowledgements

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