

New selective gas sensor based on piezoelectric quartz crystal modified by electropolymerization of a molecular receptor functionalised with 2,2'-bithiophene

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Abstract

A new gas sensor suiting the quartz crystal microbalance (QCM) technology has been realized and studied. The sensor is obtained by electropolymerization, onto the surface of a gold-coated piezoelectric quartz crystal (PQC), of a molecular receptor properly functionalised with 2,2'-bithiophene. The obtained polymeric coating has shown to be able to selectively form hydrogen bonds with organic molecules containing electronegative atoms like chloroform, acetone, ethyl acetate, ethanol even in presence of hexane or toluene which do not interact with the receptor. The easy electrosynthetic preparation and the specificity of the response are the fundamental advantages of such a polymeric films. The effectiveness of the immobilized receptor has been tested in comparison with the responses obtained with PQCs coated with unfunctionalised poly(2,2'-bithiophene). The sensor also showed good reproducibility and fairly long lifetime.

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1. Introduction

Piezoelectric quartz crystals are widely used for controlling frequency in communication equipment and have long been used as frequency and time standards. These stable devices become selective gas detectors when coated with suitable materials [1,2]. The operating principle of QCM sensors is based on the interaction between the surface of a quartz crystal coated with the sensing layer and the analytes. If a rigid layer behaviour is assumed for the crystal, the change in resonant frequency is a function of the mass changes on the surface of the PQC, according to the Sauerbrey equation [3]:

$$\Delta F = -2.26 \times 10^6 \cdot f_0^2 \cdot \frac{\Delta m}{A} \quad (1)$$

where ΔF is the observed frequency change (Hz), f_0^2 the fundamental frequency of the PQC, Δm the mass change (g) and A is the working surface area of the quartz/electrode (cm^2).

Usually, the sensing films employed as coatings for QCM sensors are empirically chosen and their deposition is classically carried out by casting techniques like Spin Coating [4], Ion Plasma [5] and Langmuir–Blodgett (LB) [6]. Although the LB is one of the most promising techniques among the above cited, this casting method requires dedicated and expensive equipment. The chemical nature of the organic sensing coatings employed for the realization of QCM sensors is very heterogeneous [7]. One of the first applications of such sensors derived from the deposition of a gas chromatographic stationary phase on the surface of PQC unit [8]. The interactions between the sensing coating and the detected analytes are usually aspecific, [9] involving bulk dissolution of organic molecules in polymeric layers, dispersion interactions, polarizability, dipolarity, etc.

In this paper, we present a QCM sensor obtained by electropolymerization, onto the surface of a gold-coated PQC,

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of a molecular receptor properly functionalised with 2,2'-bithiophene as monomeric unit.

Conjugated polymer films have been found to be suitable for sensor applications as they exhibit changes in optical or electrical properties when they interact with certain substances. These polymers include polythiophenes [10], polypyrroles [11] and polyanilines [12,13]. Functionalised polythiophenes have been found to be versatile materials with interesting electrochemical properties suitable for sensor application [14,15]. The synthesis of a customized monomer, obtained by functionalization of a molecular receptor with an electropolymerizable 2,2'-bithiophene-3-yl-hexylene unit, allowed us to realize a new gas sensor with response directly ascribable to selective and specific interactions between the analytes and the electropolymerized sensing coating. The response to vapors of nine different compounds has been evaluated in terms of structure–property relationship of the receptor, and results lead to an hypothesis on the interaction mechanism.

2. Experimental

2.1. Synthesis of 4-(6-bromohexyl)-2,2'-bithiophene (1)

The hexyldithienyl building block **1** was synthesized according to already reported procedures [16–20].

2.2. Synthesis of dimethyl 5-(6-[2,2']-bithiophenyl-3-yl-hexyloxy)-isophthalate (2)

NaH (Merck, 60%, 0.07 g, 2.90 mmol), previously washed with hexane, and **1** (0.70 g, 2.13 mmol) were added to a solution of 5-hydroxy-isophthalic acid dimethyl ester (Aldrich, 98%, 0.40 g, 1.90 mmol) in DMF (25 ml). The resulting mixture was stirred at 70 °C for 4 h, cooled at room temperature and quenched with methanol (CAUTION!). The solvent was then evaporated to dryness under reduced pressure and the solid residue taken up with ethyl acetate and 10% aqueous solution of HCl. The separated organic phase was washed with water up to neutrality, dried over Na₂SO₄ and evaporated to dryness under reduced pressure. Purification of the residue by column chromatography (hexane/ethyl acetate 8:2) afforded 0.55 g (63%) of **2** as a deliquescent solid. ¹H NMR (300 MHz, CDCl₃) δ: 1.4–1.6 (m, 2H), 1.6–1.7 (m, 2H), 1.8–1.9 (m, 2H), 2.79 (t, 2H, *J* = 7.8 Hz), 3.96 (s, 6H), 4.04 (t, 2H, *J* = 6.3 Hz), 6.95 (d, 1H, *J* = 5.1 Hz), 7.07 (dt, 1H, *J*₁ = 4.9, *J*₂ = 1.1 Hz), 7.13 (dd, 1H, *J*₁ = 4.9, *J*₂ = 1.1 Hz), 7.19 (d, 1H, *J* = 5.1 Hz), 7.32 (dd, 1H, *J*₁ = 5.1, *J*₂ = 1.1 Hz), 7.75 (bs, 2H), 8.28 (bs, 1H). ¹³C (75 MHz, CDCl₃) δ: 25.7, 28.8, 28.9, 29.0, 30.5, 52.3, 68.4, 119.7, 122.7, 123.7, 125.3, 126.0, 127.3, 129.8, 130.5, 131.6, 136.1, 139.3, 159.1, 166.1. MS-Cl(+)*m/z*: 459 [MH⁺].

2.3. Synthesis of 5-[(6-[2,2']-dithienyl)3-yl-hexyl]oxy]isophthalic acid (3)

To a solution of **2** (0.45 g, 0.98 mmol) in THF (25 ml), a 10% (w/w) aqueous solution of KOH (10 ml) was added and

the resulting reaction mixture refluxed. After 2 h, the reaction was cooled to room temperature and the THF removed under reduced pressure. The residual water solution was acidified with an excess of a 10% solution of HCl and extracted with ethyl acetate. The separated organic phase was evaporated to dryness under reduced pressure to afford **3** (95%) as a white solid which not require further purifications. ¹H NMR (300 MHz, DMSO-*d*₆) δ: 1.3–1.5 (m, 4H), 1.6–1.7 (m, 2H), 1.7–1.8 (m, 2H), 2.72 (t, 2H, *J* = 7.5 Hz), 4.04 (t, 2H, *J* = 6.6 Hz), 7.04 (d, 1H, *J* = 5.4 Hz), 7.11 (bt, 1H, *J* = 5.1 Hz), 7.13 (dd, 1H, *J*₁ = 5.1, *J*₂ = 1.1 Hz), 7.44 (d, 1H, *J* = 5.4 Hz), 7.57 (dd, 1H, *J*₁ = 5.1, *J*₂ = 1.1 Hz), 7.62 (bs, 2H), 8.06 (bs, 1H). Elemental analysis for C₂₂H₂₂O₅S₂ (calcd.): C, 61.37; H, 5.15; S, 14.89; found: C, 61.02; H, 5.85; S, 12.86; MS-Cl(+)*m/z*: 431 [MH⁺].

2.4. Synthesis of 5-[(6-[2,2']-bithiophenyl-3-yl-hexyloxy)-*N,N'*-diphenyl-isophthalamide (4)

To a solution of **3** (0.15 g, 0.35 mmol) in anhydrous DMF (25 ml), aniline (0.08 g, 0.87 mmol) and 1,3-diisopropylcarbodiimide (Aldrich, 99%, 0.11 g, 0.87 mmol) were added. The resulting reaction mixture was stirred at room temperature for 8 h, then the solvent was completely removed under reduced pressure. The crude residue was taken up with water and ethyl acetate. The separated organic phase was washed with water up to neutrality, dried over Na₂SO₄, and evaporated to dryness under reduced pressure. Purification of the residue by column chromatography (eluent CH₃OH:CH₂Cl₂ = 0.5:95) followed by a further purification with preparative TLC (eluent: CH₂Cl₂:ethyl acetate, 9:1) afforded **4** as a white powder (yield 10%). ¹H NMR (300 MHz, CDCl₃) δ: 1.3–1.4 (m, 4H), 1.6–1.8 (2m, 4H), 2.75 (t, 2H, *J* = 7.5 Hz), 3.92 (t, 2H, *J* = 6.5 Hz), 6.95 (d, 1H, *J* = 5.1 Hz), 7.07 (dt, 1H, *J*₁ = 5.1, *J*₂ = 1.1 Hz), 7.13 (dd, 1H, *J*₁ = 5.1, *J*₂ = 1.1 Hz), 7.17 (t, 2H, *J* = 7.5 Hz), 7.19 (d, 1H, *J* = 5.1 Hz), 7.32 (dd, 1H, *J*₁ = 5.1, *J*₂ = 1.1 Hz), 7.34 (t, 4H, *J* = 7.5 Hz), 7.46 (bs, 2H), 7.67 (d, 4H, *J* = 7.5 Hz), 7.78 (bs, 1H), 8.26 (s, 2H). ¹³C (75 MHz, CDCl₃) δ: 25.8, 28.9, 29.0, 29.1, 29.7, 30.5, 68.7, 116.6, 116.9, 120.4, 123.8, 124.9, 125.3, 126.1, 127.3, 129.1, 129.8, 136.9, 137.8, 139.4, 159.9, 164.9. MS-ESI(+)*m/z*: 580 [MH⁺].

2.5. Polymeric film production

The commercially available reagents were used without any further purification. Acetonitrile was dried over molecular sieves and preserved under nitrogen. The electropolymerizations and the characterization of the sensor were carried out using a potentiostat CHI 430 (CH Instrument, Texas) supplied with QCM unit, managed by dedicated software. The electropolymerizations were performed in a Teflon cell (5 ml) using QCM devices as working electrodes, a silver–silver chloride pseudoreference (with respect to which the ferrocene system showed an *E*_{1/2} = 0.402 V, calculated as mean value of cathodic and anodic peak potentials in cyclic voltammograms) as reference electrode and a platinum rod as counter electrode;

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