

Modified porous silicon for electrochemical sensor of *para*-nitrophenol



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ABSTRACT

Hybrid structures based on polythiophene modified porous silicon was used for the electrochemical detection of *para*-nitrophenol, which is a toxic derivative of parathion insecticide and it is considered as a major toxic pollutant.

The porous silicon was prepared by anodic etching in hydrofluoric acid. Polythiophene films were then grown by electropolymerisation of thiophene monomer on three different surfaces: hydrogenated PSi, oxidized PSi and amine-terminated PSi.

The morphology of the obtained structures were observed by scanning electron microscopy and characterized by spectroscopy (FTIR). Cyclic voltammetry was used to study the electrochemical response of proposed structures to *para*-nitrophenol. The results show a high sensitivity of the sensor and a linearity of the electrochemical response in a large concentration interval ranging from 1.5×10^{-8} M to the 3×10^{-4} M.

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1. Introduction

Nitrophenols (NPhs) are the most toxic organic compounds used extensively in the production of pesticides, dyes and pharmaceuticals as well in the manufacture of explosives [1,2]. NPhs may cause ecotoxicity, mutagenicity, carcinogenicity, immunotoxicity, reproductive toxicity and tumors of the urinary tract [3]. In particular, *para*-nitrophenol (p-NPh) is a toxic derivative of parathion insecticide and it is known to be hazardous waste which enters the environment from sewage and agricultural water. In addition, it is soluble and stable in water, so it can affect soils and humans. Inhalation or ingestion of p-NPh by humans causes headaches, drowsiness, nausea, and cyanosis (blue color in lips, ears, and fingernails). Therefore, there is an urgent demand to develop analytical and simple devices to monitor p-NPh for environmental control and protect human health.

Some noticeable detection techniques such as chromatography and spectrophotometry have been employed to determine the presence of nitrophenol and its derivatives [4–8]. However, these methods require special sample preparation, are time consuming and are complex and expensive. While the electrochemical methods are simple operations, give fast response and can provide a fair degree of sensitivity and selectivity [9,10]. Moreover, organic/inorganic hybrid materials were a subject of intense investigation due to the potential applications of these structures in chemical and biological sensors [11]. In this framework, the coating of different materials with conducting electroactive polymers such as polyaniline, polypyrrole, polythiophene and their derivatives has attracted special attention [12,13]. In this work, porous silicon (PSi)/polythiophene (PTH) hybrid structures were prepared as a device for the electrochemical detection of p-NPh. PSi is an interesting material for sensing applications due to its high surface area. However, its stability in air over time remains poor leading to the degradation of the optical and electronic properties of the material. Several methods have been used to stabilize PSi surface for a better chemical control of this material by replacing Si–Hx bonds with stronger Si–C or Si–O–C bonds [14,15]. In this work, PTH was used to stabilize PSi surface. PTH is an interesting class of conducting polymers due to its stability in different environments. Furthermore, this conducting polymer confers to PSi innovative and

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improved properties. Indeed, conductive polymers allow charge transfer improvement and ensure continuity in the conduction mechanism for a better detection.

PTh was deposited by electrochemical polymerization [15,16] of thiophene monomer. This method offers several advantages such as simplicity and rapidity. In this study, the polymer was deposited on hydrogen-terminated PSi, amine-terminated PSi and on oxidized PSi substrates. The hybrid structures thus obtained combine the high surface area of PSi with the outstanding properties of PTh for the electrochemical detection of p-NPh.

The novelty of this work is in the use for the first one the simple and inexpensive hybrid structures composed by porous silicon and polythiophene for electro-detection of p-NPh. These sensors are easy to achieve. A good protection of their surfaces by a conductive polymer provides a good stability over time.

2. Experimental

2.1. Materials

Silicon wafers were purchased from Siltronics. Hydrofluoric acid 40% (HF) was supplied by Amplex. All other chemicals are reagent grade or higher and were used as received unless otherwise specified. Milli-Q water (18 M Ω) was used for all experiments. Amino-propyltrimethoxysilane (APTMS), acetonitrile and tetrabutylammonium tetrafluoroborate 99% were all available from Aldrich. All experiments were performed in 0.1 M phosphate buffer solution (PBS) with pH = 7.

2.2. Fabrication of hybrid structures

2.2.1. PSi preparation

Silicon wafers used in these experiments are 500 μ m thick, double-side polished, (100) oriented and boron-doped (p-type) with a resistivity of 0.05–0.10 Ω cm, they were first cleaned in 3:1 concentrated H₂SO₄/30% H₂O₂ for 20 min at 80 °C and then rinsed copiously with Milli-Q water. The clean wafers were immersed in 48% aqueous HF solution for 1 min at room temperature to remove the native oxide. The hydrogen-terminated surfaces were electrochemically etched for 30 seconds in 1:1 (v/v) solution of pure ethanol and 48% aqueous HF, at a current density of 80 mA cm⁻². After etching, the samples were rinsed with pure ethanol and were dried under a stream of dry nitrogen.

2.2.2. Oxidation

The hydrogen-terminated PSi surfaces were oxidized in an oven at 200 °C for 24 h.

2.2.3. Amine termination

Surface amination was performed by reaction of oxidized PSi surface with 3% APTMS in ethanol/water: 95/5 (v/v) for 60 min under sonication. The resulting surfaces were then washed with isopropanol, twice in water, then in methanol and finally annealed at 120 °C for 20 min.

2.2.4. Fabrication of PSi/PTh structures

In this work, three types of PSi/PTh hybrid structures were elaborated. In the first one, thiophene was directly electropolymerised on hydrogen-terminated PSi surface. In the second structure, the electropolymerisation was made on oxidized PSi surface and in the last one; PTh was grown on oxide/APTMS/PSi surface.

Electrochemical polymerization of thiophene on PSi surfaces was performed in CH₃CN Bu₄NBF₄ (0.1 M) solution containing 0.05 mM thiophene, by sweeping the potential between -1 V and +4 V at a scan rate of 50 mV s⁻¹. Electrochemical cell with three electrodes was used comprising PSi substrate as working electrode

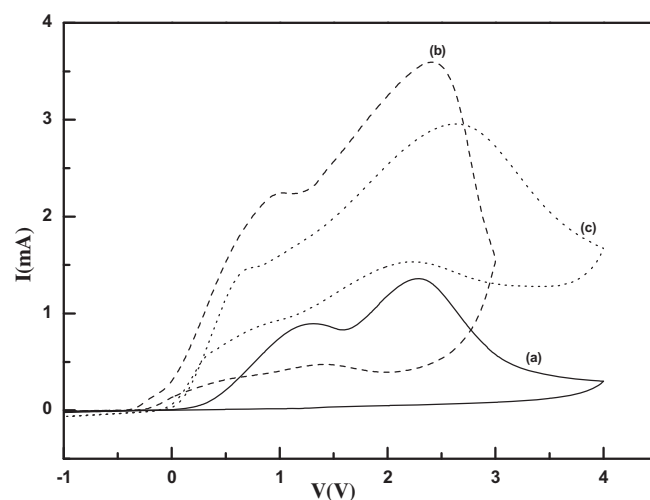


Fig. 1. Cyclic voltammograms corresponding to the anodic electropolymerization of thiophene monomer on: (a) PSi surface, (b) oxide/PSi surface, (c) APTMES/oxide/PSi surface.

and platinum wire as counter electrode. All potentials are relative to 0.01 M Ag⁺/Ag system.

2.3. Surfaces characterization

The structures were analyzed by FouFTIR spectroscopy with a ThermoNicolet Nexus 670 apparatus at a resolution of 4 cm⁻¹ and 32 scans. Surface morphology of the hybrid structures was investigated by scanning electron microscope (SEM) PHILIPS 505. Electrochemical experiments were performed using a potentiostat galvanostat VMP3. The sample was mounted in a PTFE holder with a copper contact. A platinum wire was used as counter electrode and all potentials were relative to 0.01 M Ag⁺/Ag system.

3. Results and discussion

3.1. Electrochemical polymerization

Fig. 1a shows the cyclic voltammogram of thiophene electropolymerization on PSi surface. The onset of thiophene oxidation occurs at 1.26 V corresponding to the creation of first active centers at electrode surface. The second oxidation appears at 2.28 V corresponding to the bipolaron structure of PTh.

Thiophene electropolymerization on oxidized PSi surface and on APTMES/oxide/PSi surface was realized by the same technique used to deposit PTh on PSi surface. The oxidation potential has shifted to low potential at 0.97 V for oxidized PSi surface (Fig. 1b) and at 0.67 V for APTMES/oxide/PSi (Fig. 1c), due to the change of the surface state.

3.2. FT-IR spectroscopy analysis

FTIR spectroscopy was used to characterize the changes associated with the surface composition upon PSi functionalization. FTIR spectrum of a freshly prepared PSi surface (Fig. 2a) exhibits a typical tripartite bands corresponding to Si–H_x (x = 1, 2, 3) stretching modes (2087 cm⁻¹ for ν Si–H, 2115 cm⁻¹ for ν Si–H₂ and 2137 cm⁻¹ for ν Si–H₃). The Si–H₂ bending mode is visible at 908 cm⁻¹. Fig. 2b exhibits bands between 3200 and 2840 cm⁻¹ corresponding to C–H stretching vibrations of thiophene and its bending vibrations appear between 1450 and 1300 cm⁻¹. The band at 1660 cm⁻¹ is attributed to C=C stretching vibration. A broad band is observed at 1082 cm⁻¹, corresponding to C–H bending vibration of thiophene

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