



Highly selective and sensitive simple sensor based on electrochemically treated nano polypyrrole-sodium dodecyl sulphate film for the detection of para-nitrophenol

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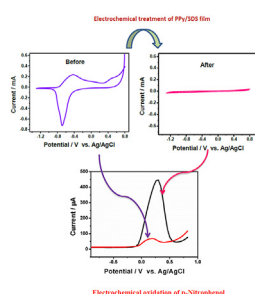
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HIGHLIGHTS

- An electrochemically treated nano polypyrrole/sodium dodecyl sulphate film modified glassy carbon electrode was prepared and applied for determination of *p*-NP.
- A very good linear detection range (from 0.1 nM to 100 μ M) was obtained.
- The best LOD (0.1 nM) of *p*-NP was obtained, without any interference.

GRAPHICAL ABSTRACT



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ABSTRACT

An ultrasensitive and highly selective electrochemical sensor for the determination of *p*-nitrophenol (*p*-NP) was developed based on electrochemically treated nano polypyrrole/sodium dodecyl sulphate film (ENPPy/SDS film) modified glassy carbon electrode. The nano polypyrrole/sodium dodecyl sulphate film (NPPy/SDS film) was prepared and treated electrochemically in phosphate buffer solution. The surface morphology and elemental analysis of treated and untreated NPPy/SDS film were characterized by FESEM and EDX analysis, respectively. Wettability of polymer films were analysed by contact angle test. The hydrophilic nature of the polymer film decreased after electrochemical treatment. Effect of the pH of electrolyte and thickness of the ENPPy/SDS film on determination of *p*-NP was optimised by cyclic voltammetry. Under the optimised conditions, the *p*-NP was determined from the oxidation peak of *p*-hydroxyaminophenol which was formed from the reduction of *p*-NP in the reduction segment of cyclic voltammetry. A very good linear detection range (from 0.1 nM to 100 μ M) and the best LOD (0.1 nM) were obtained for *p*-NP with very good selectivity. This detection limit is below to the allowed limit in drinking water, 0.43 μ M, proposed by the U.S. Environmental Protection Agency (EPA) and earlier reports. Moreover, ENPPy/SDS film based sensor exhibits high sensitivity ($4.4546 \mu\text{A } \mu\text{M}^{-1}$) to *p*-NP. Experimental results show that it is a fast and simple sensor for *p*-NP.

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1. Introduction

Nitroaromatic compounds are used in the manufacturing of

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dyes, plasticizers, pesticides, fungicides and explosives [1]. In particular, *p*-nitrophenol (*p*-NP) is one of the nitrophenols cited in the list of priority pollutants of the U.S.A. Environmental Protection Agency (EPA) due to its toxicity (carcinogen, teratogenic and mutagenic) and persistence [2,3]. The harmful effects of *p*-NP on humans include headache, fever, breathing trouble and even death at high levels of exposure [4]. The *p*-NP is one of the examples that can be found in wastewater and agricultural run-off due to biodegradation of parathion and methyl parathion [5]. This chemical compound is an inhibitor of acetylcholinesterase [6]. Furthermore, the *p*-NP is a usable model chemical pollutant in the elaboration of biodegradability tests due to its erratic biodegradability. The *p*-NP exists not only in industrial wastewater but also in freshwater and marine environments [7,8].

The permissible limit of *p*-NP in the environment by different agencies like United States EPA and the European Commission are 0.43 μM and 0.72 nM, respectively [9]. Thus, there is a need to develop simple and reliable sensing devices for the determination of trace amounts of *p*-NP in the environment. Hitherto, various methods have been employed for sensitive detection of *p*-NP including spectrophotometry [10,11], high performance liquid chromatography [12–15], fluorescence [16–18] and electrophoresis [19–22]. However, these approaches involve complex sample preparation procedures and generally require expensive instrumentation. On the other hand, electrochemical methods have received considerable attention in the determination of *p*-NP, because of their great advantages, such as simple operation, inexpensive, fast response and in situ detection [23,24]. Different modified electrodes have been used for sensitive detection of *p*-NP such as carbon nanotubes, metal NPs, and conducting polymers [25–28]. Zhang et al., reported a novel method for simultaneous determination of NP isomers at nano-gold modified glassy carbon electrode [29]. However, No report is available for the detection of *p*-NP using PPy film in the literature.

In this work, a new and simple sensing material was developed for designing a highly selective and sensitive electrochemical sensor for *p*-NP. This new modified electrode paves a way to the potential application for electrochemical detection of picomolar level of *p*-NP. To the best of our knowledge, this modified electrochemical sensor represents the best low detection limit, higher sensitivity and wide linear detection range than the other sensors reported earlier. Well-separated square wave voltammetric peaks were observed for *p*-NP and *o*-NP during simultaneous determination.

2. Experimental

2.1. Materials and equipment

All chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with doubly distilled water. *p*-NP, *o*-NP, Pyrrole monomer, Sodium dodecyl sulphate (SDS), Lithium perchlorate (LiClO_4), Sodium hydroxide, disodium hydrogen phosphate (Na_2HPO_4), monosodium dihydrogen phosphate (NaH_2PO_4), potassium chloride and sodium acetate were purchased from Sigma–Aldrich. Potassium ferricyanide and ferrocyanide were purchased from Merck. Phosphate buffer solution (PBS, 0.1 M, pH = 7) was prepared from NaH_2PO_4 and Na_2HPO_4 salts. The 10 mM stock solutions of *p*-NP and *o*-NP were prepared by using doubly distilled water. Both the Nitrophenol solutions in low concentration were prepared just before using.

Cyclic voltammetry (CV) and Square wave voltammetry (SWV) measurements were performed using Bio-logic Science Instruments (Model: SP-150 s/n 0555 electrochemical workstation). The cell setup contained a glassy carbon electrode (GCE) (3 mm) as

working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and Pt wire as counter electrode. The pH measurements were carried out with Cyberscan 510 pH meter EUTECH instrument, Singapore. The surface morphology of the polymer films were studied using Zeiss FESEM. EDAX analysis with Bruker Quantx EDS detector. Wettability was studied using the contact angle Data physics instrument.

2.2. Electro chemical preparation of ENPPy/SDS film

The GC electrode was polished using 0.05 μm alumina powder followed by rinsing thoroughly with doubly distilled water. After successive sonication in 1:1 acetone and double distilled water, and dried at room temperature. The electrochemical polymerization was carried out in solution containing 0.1 M pyrrole, 0.01 M SDS and 0.05 M LiClO_4 in the potential range from -0.40 V to 0.75 V at scan rate of 50 mV s^{-1} . Then the above modified electrode was electrochemically treated in 0.1 M phosphate buffer solution (pH 7.0) by scanning between 0.80 V and -1.30 V for several cycles until to get very stable background current. Then, the electrode surface was washed with distilled water.

3. Results and discussion

3.1. FESEM images of NPPy/SDS film and ENPPy/SDS film

The surface morphologies of the NPPy/SDS film (before cycling) and ENPPy/SDS film (after cycling in phosphate buffer solution) were characterized by FESEM (Fig. 1). As shown in Fig. 1A–D, the NPPy/SDS film and ENPPy/SDS film exhibit a similar morphology such as globular structure, but the size of the polymer particle decreases after electrochemical treatment and more over nano size cracks are also formed in the polymer matrix. This morphological change must be due to that the replacement of macro size SDS ions by smaller phosphate ions during dedoping may create nano cracks [30].

3.2. Elemental analysis of NPPy/SDS film and ENPPy/SDS films

The elemental analysis of the NPPy/SDS film and ENPPy/SDS films were analysed by EDX technique (Fig. 2A and B). In the spectrum of NPPy/SDS film, the peaks for sulfur and sodium are appeared which indicate that SDS ions have been successfully incorporated in the PPy-matrix during electropolymerization. However, the amount of sulfur atoms decreased from 0.81 atomic % to 0.29 atomic % after electrochemical treatment. Similarly, oxygen atom increases from 13.21 atomic % to 24.03 atomic % and carbon atoms decreases from 59.68 atomic % to 45.33 atomic % which indicates that the SDS ions must be expelled by phosphate ions during cycling in the phosphate buffer solution. Moreover, interestingly the EDX spectra shows peak for phosphorous in the ENPPy/SDS film. Thus, the results support the replacement of the SDS ions by phosphate ions.

3.3. Ion exchange properties of the NPPy/SDS film

Oxidation of “conducting polymers” generates fixed positive charges on the polymer back bones. In the reduced state, the PPy matrix is electrochemically neutral. The neutral PPy films are therefore relatively poor ionic conductors in addition to poor electronic conductors. To alter this situation, a number of polymer structures have recently been synthesised which contain electro-inactive molecules with fixed negative charges. This has been achieved mainly by electropolymerizing pyrrole in the presence of macro anions like poly (styrene-sulfonate), poly-(vinylsulphate),

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