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An Electrochemical Sensor Platform for Sensitive Detection of Iron (III) Ions Based on Pyrene-Substituted Poly(2,5-dithienylpyrrole)

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Conducting polymers, which have a great potential for use in many technological application areas, can be used to design new selective, sensitive, highly efficient and practical sensor platforms. Herein, a pyrene-substituted 2,5-dithienylpyrrole (TPP) has been synthesized and its conductive polymer has been coated electrochemically on the ITO electrode surface to form a new sensor platform. After electrochemical and surface characterization of conducting polymer based sensor platform, its electrochemical responses to different metal ions have been investigated in aqueous media. It has been determined that P(TPP) displays excellent potentiometric response to Fe(III) ions while there is no significant electrochemical signal observed in other metal ion solutions including Fe(II), Zn(II), Cu(II), Hg(II), Cd(II). P(TPP) sensor platform has exhibited high stability, sensitivity, reproducibility toward the determination of Fe(III) with a good detection limit of 1.73×10^{-7} M. The sensor platform has great potential for disposable low-cost metal ion sensing platform which is convenient in-field testing application could be used in aqueous and biological samples.
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Iron is a certain requirement for most of life including humans and most bacterial species. It plays a vital role as oxygen transporter in human body. Besides, it has important effect on the regulation of cell growth.[1,2] But an excess of iron ions can lead to toxicity and even death. Thus, the development of simple, selective and rapid method for the determination of the iron ions is of great importance.

There are several analytical techniques including, atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) have been reported for the determination of metal ions.[3–11] Even though, these techniques required sophisticated instruments and long time for analysis, most of the above techniques have been widely utilized for the determination metal ions during the past decades. However, electrochemical methods have gained a great importance for detection of metal ions depends on their sensitivity, simplicity, low cost, and rapidity. The smart electrochemical methods can be absolutely a good alternative to complicated analytical techniques, because it allows selective determination of components without the need for expensive and complicated equipment.

Recently, the design and application of conducting polymers (CPs)[12–17] for the fabrication of electrochemical sensor platforms to use determination of metal ions have attracted great interest because of their mechanical, optical and electrical features in addition easily synthesizable, low cost and stability.[17–25]

For example, M. A. Deshmukh et al. have reported, conducting polymer based electrochromic film electrode, which was fabricated by electrochemical polymerization of aniline monomer on indium tin oxide (ITO) covered glass electrodes in order to produce metal ion sensor prototype. Both chronoamperometric and electrochromic detection of Cu(II) ions have been successfully investigated by using PANI/ITO-electrodes.[26] In another study, C. Kaewtong et al. have reported rhodamine-appended polyterthiophene network thin film which was electropolimerized on ITO electrode. The ion selective potentiometric responses of the sensor film have been tested for various metal ions. It has been found that the conducting polymer based sensor platform demonstrated selectivity to Hg(II) ions.[27] As a result, recent studies have been showed that ITO-glass electrodes modified by conducting polymers have been used in the design of electrochemical metal ion sensors.

The important advantages of electrochemical sensors based on CPs over other existing methods are that CPs are capable of exhibiting improved response properties including fast response to analytes and simple preparation. Besides, since conducting polymer films are insoluble in organic solvents, their sensor lifetime is long. Among the best known conductive polymers, polypyrroles, polythiophenes and polycarbazoles have potential usage in many technological applications[28–34] such as sensors,[35–39] electrochromic devices,[40–44] supercapacitors,[45] fuel cell[46,47] and solar cells.[48–51]

Due to limitations and shortcomings of existing detection techniques, the new metal detection techniques to be implemented using new materials will be quite exciting. Therefore, in this study, different approaches based on conductive polymers for the determination of iron ions have been introduced. For this purpose, pyrene substituted thienyl-pyrrole derivate (TPP) has been synthesized and electrochemical polymerized on ITO glass. The electrochemical and surface characterization of the P(TPP) film has been investigated via cyclic voltammetry and AFM studies. P(TPP) based conducting polymer film has been used as solid state sensor platform to selective and sensitive determination of Fe(III) ions over the other metal ions such as Fe(II), Zn(II), Cu(II), Hg(II), Cd(II). Most of the published studies are focus on molecular sensor studies based on changing UV or fluorescence intensity of the solution with the interaction of small molecules and metals in solution phase. To the best of our knowledge, no paper has reported on determination of Fe(III) ions using solid-state conducting polymer film. With this study, Fe(III) ions sensing platform based on solid-state conductive polymer film has been designed and characterized. Thus, the low-cost, suitable for on-site sensitive testing, multi-used, sensitive and selective Fe (III) ion sensor platform has been designed for the first time.

Experimental

Apparatus and chemicals.—Electrochemical experiments were carried out with a potentiostat/galvanostat (Ivium). Electrochemical cell consisted of three electrode which are indium tin oxide (ITO)-coated glass (Thicknesses: $7 \times 50 \times 0.5$ mm, surface resistivity: 8–12 Ω/sq) as working electrode, a platinum wire as counter electrode and Ag wire as reference electrode (calibrated against ferrocene Fc/Fc+ redox couple $E_{1/2} = +0.35$ V).

Surface characterization of the P(TPP) film on ITO electrode was performed on Nanomagnetics Instruments Atomic Force Microscope (hp-AFM). The structural characterization of the monomer (^{1}H-NMR) was performed on 400 MHz/54 mm Ultra Shield plus model spectrometer.

The structural characterization of P(TPP) film and propose sensing mechanism of P(TPP)+Fe(III) ions have been explained by Fourier Transform Infrared Spectroscopy (Perkin-Elmer 2000 FTIR spectrometer 4000–400 cm^{-1} with a resolution of 4 cm^{-1}) with a Universal ATR Polarization. P(TPP) and P(TPP)+Fe(III) samples in the solid form have been placed directly on the top plate of FTIR-ATR spectrometer.

For the synthesis of monomer TPP, all necessary materials such as; succinyl chloride, toluene, hydrochloric acid, toluene, thiophene, aluminum chloride, ethanol, 1-pyrenecarboxaldehyde, magnesium sulfate were purchased from Sigma Aldrich. For electrochemical

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