Journal of Atomic and Molecular Sciences

Global Science Press

A novel imprinted electrochemical sensor for dopamine determination based on electron conductivity enhanced by ferrocenyl chalcone derivative film

Liming Chen[a], Defang Liu[a,b,c*], Caixia Wang[a]

Abstract. A novel biochemical sensor based on molecular imprinted technology was built through electropolymerization. One of the keystones of the technology is the discovery and application of new conductive polymer. Herein, a new conductive ferrocenyl chalcone derivative: [1-Oxo-3-(3-thienyl)-2-propen-1-yl] ferrocene (OTPylFc) was synthesized and characterized by nuclear magnetic resonance (NMR) and finally adopted in the technology. The OTPylFc and pyrrole mixture was eletropolymerized in this work and showed satisfying result in improving current peaks. The linear relationship was 1.729×10^{-6} M to 6.916×10^{-4} M. It is believed that the structure and their conductive analogs formed co-polymers would have a promising prospect in future research.

Keywords: OTPylFc; Molecular Imprinted Technology; DPV; Electrochemical Sensor;
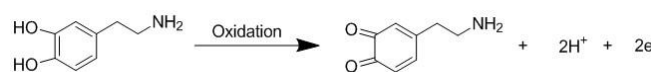
1.   Introduction

Electropolymerization technique has been used in various electro-conductive monomers such as benzene ring, five-membered heterocycle, alkynes and alkene to fabricate conducting polymers. Among which, polypyrrole (PPy) is one of the most extensively used for it can be easily deposited electrochemically onto a variety of substrate materials forming a stable film and can be used in a neutral pH region[1]. A stable electro-conductive membrane could be ideal candidates for substrate on electrochemical sensor, however, in most instances, the membrane can't show any signals to analysis. Molecularly imprinted polymers (MIPs) technique was brought in to tackle the analysis recognition problem. Generally, MIPs are thin films copolymerized by functional monomers and crosslinked with target molecules. Molecular templates formed via polymerization and elution. Finally, a complementary cave is obtained which shows specific affinity to original molecule. It is reported that the mechanism of MIPs technique is somehow like antigen-antibody or key-lock recognition[2]. Thus, MIPs technique endows the films specific recognition ability and broaden the application of electro-conductive films. It is reported that monomers, such as ethacridine[3], nicotinamide[4], o-aminophenol[5], or monomer mixtures[6] could be applied in DA determination by MIPs technology and showed satisfying results. Nevertheless, Shabi Abbas Zaidi pointed out that MIPs sensors having been typically suffered from low sensitivity for the lacking of conductivity and electrocatalytic activity[7]. An effective way

to deal with this problem is to find some conductive materials to be a mediator. Ferrocenyl chalcone derivative was chosen as the mediator in this work.

2.   Experimental

2.1 Reagents and chemicals

3-Thiophenecarboxaldehyde (ThCA>97%) was purchased from Titan (Shanghai, China). Tetra-n-butylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$), and Acetylferrocene (AcFc) were provided by Beijing bailingwei Technology Co. (Beijing China). Sodium dihydrogen phosphate (NaH$_2$PO$_4$), disodium hydrogen phosphate (Na$_2$HPO$_4$) ethanol (EtOH) acetonitrile (MeCN) and sodium hydroxide (NaOH) were bought from Chongqing Chuandong Chemical (Group) Co., Ltd. HNO$_3$, 98% H$_2$SO$_4$, ascorbic acid (AA), urid acid (UA), dopamine (DA), potassium chloride (KCl), and pyrrole (Py) were purchased from Aldrich and all reagents used in experiments were of
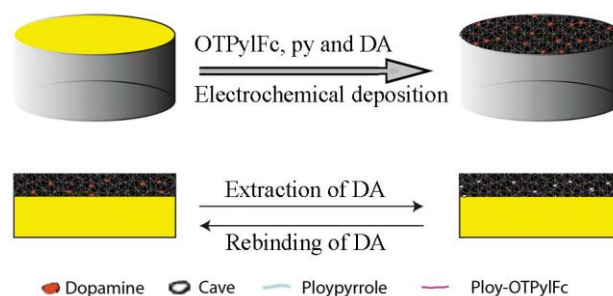

Scheme 1 The oxided process of DA.

Figure 1. Sketch of organic monomers forming polymers and the process of DA extract and rebind with the polymers.

a. School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China
b. Key Laboratory of Applied Chemistry of Chongqing Municipality, Institute of Bioorganic and Medicinal Chemistry, Southwest University, 400715, China
c. Key Laboratory of Biorheological Science and Technology, Ministry of Education, College of Bioengineering, Chongqing University, No.174, Shapingba Main Street, Chongqing, 400030, China
   Corresponding authors: E-mail address: youya_liu@163.com

analytical grade and without further purification. All aqueous solutions were prepared by ultrapure water.

2.2. Apparatus

The ploy-Ferrocenyl chalcone-pyrrole (OTPylFc-Py) was characterized by a field emission scanning electron microscope (FESEM) using a JSM-7800Foperated at 20 KeV. ^{1}H NMR and ^{13}C NMR spectra (Bruker Avance 600 spectrometer) were used to ensure the structure of [1-Oxo-3-(3-thienyl)-2-propen-1-yl] ferrocene. All electrochemical experiments, cyclic voltammetry and differential pulse voltammetry included, were performed on a LK 2006AZ electrochemical workstation (Tian-jin Lanlike Co., China) with a widely used conventional three electrodes system: golden electrode modified with PFcCP as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode. All potential values were given below versus the saturated calomel reference electrode. OTPylFc was prepared in microwave reactor (MAS-, sineo microwave tecknology co. Ltd. Shanghai, China), and monitored by TLC with silica gel coated plates.

2.3 Synthesis of OTPylFc

OTPylFc was synthesized according to Aldol reaction. Briefly, AcFc (456 mg), ThCA (250 mL) and NaOH (160 mg) were dissolved in 2 mL EtOH by a three-neck round-bottom flask, then stirred vigorously for 5 min. The reaction was carried out in the microwave reactor (P=200 W) in 40 ℃ for 5 min. When the reaction was finished, the mixture was extracted in a separatory funnel, then washed with water and saturated NaCl solution for 3 times, respectively. Finally, the washed oil was condensed by rotary evaporator and separated by silica gel column chromatography.

1H NMR (600 MHz, Chloroform-d): δ (ppm) = 7.79 (d, J = 15.5 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.46 – 7.41 (m, 1H), 7.39 (dd, J = 5.2, 2.8 Hz, 1H), 6.95 (dd, J = 15.5, 1.2 Hz, 1H), 4.90 (d, J = 1.7 Hz, 2H), 4.58 (d, J = 1.7 Hz, 2H), 4.21 (d, J = 1.2 Hz, 5H).

13C NMR (151 MHz, CDCl3): δ (ppm) =193.12, 138.35, 134.39, 128.33, 126.89, 125.24, 122.74, 80.62, 72.69, 70.09, 69.69.

2.4 Preparation of OTPylFc-Py modified golden electrode (OTPylFc-Py/GE)

The golden electrode was polished with 0.05 μm alumina slurries on polish cloth, then washed in ultrasonic with ultrapure water, ethanol (1:1/V:V), HNO_3 (1:1/V:V) and ultrapure water, respectively. Finally, reduced in 1 M H_2SO_4 solution for 15 circles by cyclic voltammetry until the peak
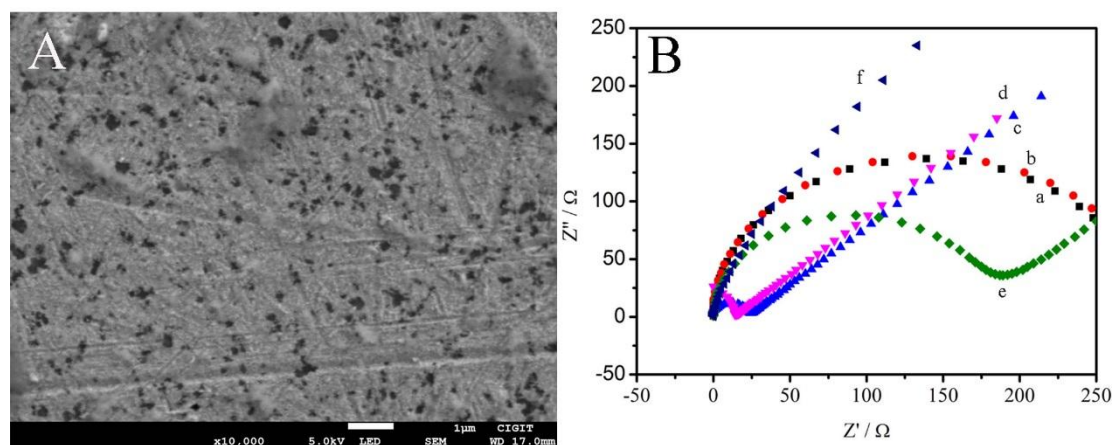

Figure2. (A) SEM of MIP/GE after washed by acetonitrile and water. (B) EIS recorded in a 0.01 mol/L $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ solution: (a) Bare golden electrode; (b) OTPylFc and DA coploy; (c) OTPylFc, pyrrole and DA co-ploy; (d) only OTPylFc ploy; (e) pyrrole and DA; (f) OTPylFc, pyrrole and DA co-ploy and then washed.
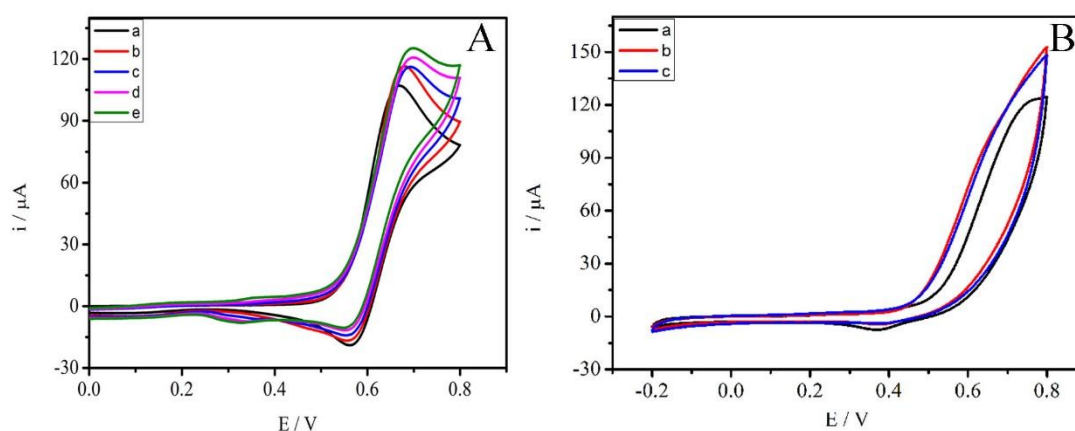

Figure 3. (A) Differential pulse voltammetry for the DA determination. (B)Analytical curve constructed from DPV of (a) 6.916×10^{-4} M; (b) 3.458×10^{-4} M; (c) 6.915×10^{-5} M; (d) 1.383×10^{-5} M; (e). 6.916×10^{-6} M; (f) 3.456×10^{-6} M; (g) 1.729×10^{-6} M.