



Research Paper

Molecularly imprinted electrochemical sensor prepared on a screen printed carbon electrode for naloxone detection



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ABSTRACT

Naloxone (NLX) is a pharmaceutical used as opioid antagonist. A molecular imprinted polymer electrochemical sensor for simple and rapid detection of NLX was prepared through the modification of commercial available screen printed carbon electrode (SPCE). The SPCE was modified with multi-walled carbon nanotubes (MWCNT) by drop coating to increase the signal response and improve the sensitivity. The MIP preparation was carried out via in situ electropolymerization using 4-aminobenzoic acid (4-ABA) as functional monomer. The morphology of the obtained sensor was characterized by scanning electron microscopy (SEM). Several parameters controlling the preparation and performance of the MIP sensor were studied and optimized. The electrochemical behavior of NLX at MIP and control non-imprinted (NIP) sensor was evaluated by differential pulse voltammetry (DPV), demonstrating a better MIP response and the success of the imprinting. The proposed MIP/MWCNT/SPCE sensor showed a linear relationship between peak current intensity and NLX concentration in the range between 0.25 and 10.0 μM , with limits of detection (LOD) and quantification (LOQ) of 0.20 μM and 0.67 μM respectively. The repeatability and reproducibility were also tested with relative standard deviations (RSD) of 4.6 and 9.6% respectively. Moreover, the applicability of the method was successfully confirmed with detection of NLX in biological samples (urine and human serum). The sensor is promising to be used for screening NLX in point-of-care people with opioid overdose.

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1. Introduction

Opioid dependence is a neurobehavioral syndrome, affecting millions of people worldwide, characterized by the repeated, compulsive seeking and use of an opioid despite adverse social, psychological, and/or physical consequences [1]. Naloxone (NLX), is a derivative of morphine and a specific opioid antagonist at mu, kappa, and delta opioid receptors [1,2] with as high affinity for opiate receptors without activate then [3]. It reverses the action of many narcotic drugs, including heroin, and thus can be used in the treatment of overdoses.

Several analytical methods have been reported for the determination of NLX mainly by high performance liquid chromatography (HPLC) [4] specially coupled with MS detection [1,5–9]. Since NLX molecules can be easily oxidised, liquid chromatography with electrochemical detection was also used [10–12]. However, this methods are costly, time consuming due to extensive sample

preparation and producing large amounts of liquid waste witch is not suitable for a green chemistry laboratory. Recently a sensor based on potentiometric measurement was described [13].

Screen-printing technology is a well-established technique that allows the production of disposable biosensors and chemical sensor [14]. The screen printed electrodes (SPE) are simple, low cost, portable, small sized and capable of mass production [15]. The reduced size of the SPEs lowers the sample volume down to 30–40 μL , which is advantageous especially in the analysis of biological samples and can be easily integrate in miniaturized portable devices [16]. The SPEs are very versatile since the composition of the printing inks could be modified with several substances such as metals, enzymes, polymers or complexing agents [17]. Otherwise deposition of different agents on the surfaces of manufactured electrodes could also be easily achieved such as molecular imprinted polymers [17–19].

Molecularly imprinted polymers (MIPs) are synthetic materials with artificially generated recognition sites capable of specifically binding a target molecule, mimicking natural receptor systems including antibodies, hormones and enzymes. MIP are prepared by a process that involves a formation of a complex between the

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functional monomers and the target molecular (template) and followed by a polymerization in the presence of a crosslinking and a solvent (porogen). Finally the template is removed and a polymeric matrix with specific cavities complementary in size, shape and functionality are produced. MIPs are ease to prepare, low cost, and show high chemical and mechanical stability. They have found applications in several different areas, such as purification and separation, catalysis, sensors, drug delivery systems [20–24]. Due to their high affinity toward the template molecule they are excellent tools to be used as selectivity elements with the construction of sensors. The main difficulty consists in the integration of the polymer with the transducer. Initially, MIPs were prepared normally by free radical polymerization and in most of cases a bulk polymer was obtained, which results in poor compatibility with the transducer and limited mass transport and rebinding kinetics. Several approaches have proposed for in situ preparation directly on the transducer surface, such as: drop-coating of a solution of a pre-prepared polymer, spin-coating, electropolymerization, grafting, and layer by layer deposition [25]. Electropolymerization has proved to be an excellent choice especially in the preparation of MIP electrochemical sensors [25–28]. It allows an ease control of polymers thickness and morphology, is highly reproducible and permits polymerization and operation in water solutions. Otherwise the use of initiator and cross-linking is normally dispensed [29].

In the present work, a novel MIP electrochemical sensor for NLX detection was constructed by electropolymerization of 4-aminobenzoic acid (4-ABA) on the surface of SPCE modified with multi-walled carbon nanotubes (MWCNT). To the best of our knowledge this is the first report of the preparation of a MIP toward NLX molecules. The combination of electropolymerization for MIP preparation with SPCE technology can be an excellent choice to ease and low cost fabrication of electrochemical sensors with high potential by applied to commercial analytical solutions.

2. Experimental

2.1. Reagents

Naloxone hydrochloride dehydrate (NLX), 4-aminobenzoic acid (4-ABA), ascorbic acid, glucose, urea, Naltrexone and Noroxymorphone hydrochloride were obtained from Sigma-Aldrich. Multi walled carbon nanotubes (MWCNTs) functionalized with $-\text{COOH}$ groups (DropSens) were prepared in *N,N*-dimethylformamide

(DMF, Sigma-Aldrich). Stock solutions of NLX (50 mM) were prepared in water and stored at 4 °C. Daily working solutions of NLX with different concentrations were prepared. Phosphate buffer solutions were prepared from KH_2PO_4 (Riedel-de Haën) and K_2HPO_4 (Riedel-de Haën) and the pH adjusted with HCl or NaOH 1 M solutions. All commercially available reagents were of analytical grade and were used without further purification. All solutions were prepared using ultrapure water (resistivity = 18.2 $\text{M}\Omega\text{ cm}$), obtained from a Millipore (Simplicity 185) water purification system. Human serum from male AB plasma was obtained from Sigma-Aldrich.

2.2. Apparatus

All electrochemical experiments were carried out with an Autolab PGSTAT 204 potentiostat-galvanostat controlled by Nova 1.10 software (Metrohm Autolab). Screen printed electrodes (DropSens, DRP-110) with working ($d = 4\text{ mm}$) and auxiliary electrode of carbon, and a reference electrode of Silver were used. The surface of the working electrode was modified to prepare the MIP/MWCNT/SPCE.

2.3. Sensor fabrication

The preparation of MIP on SPCE as obtained by electropolymerization using cyclic voltammetry. The stepwise construction process is illustrate in Fig. 1. Prior to modification a bare SPCE was rinsed with distilled water and then activated in 0.5 M H_2SO_4 by cycling the potential between -0.2 V and $+1.3\text{ V}$ at 100 mV/s during 5 cycles.

A suspension containing 2 mg of MWCNT in 1 mL DMF was prepared, sonicated for 2 h and diluted with an ultrapure water/DMF mixture (50:50), to obtain a final concentration of 1 mg/mL. A MWCNT/SPCE was prepared by deposition of 4 μL on the working electrode's surface of the prepared MWCNT suspension. The electrode was allowed to dry at room temperature and thoroughly washed with ultrapure water. A drop of 40 μL of the polymerization solution (40 mM 4-ABA, 0.5 mM NLX in phosphate buffer solution) was placed in the MWCNT/SPCE and cyclic voltammetry (CV) was performed in the potential range from -0.20 V to $+1.00\text{ V}$ at a scan rate of 100 mV/s for 20 cycles. After that, 40 μL of methanol/HCl 0.1 M (50:50) solution were consecutively placed and replaced each 5 min on the surface of the sensor during 40 min. This procedure permits the removal of the entrapped NLX molecules and produces

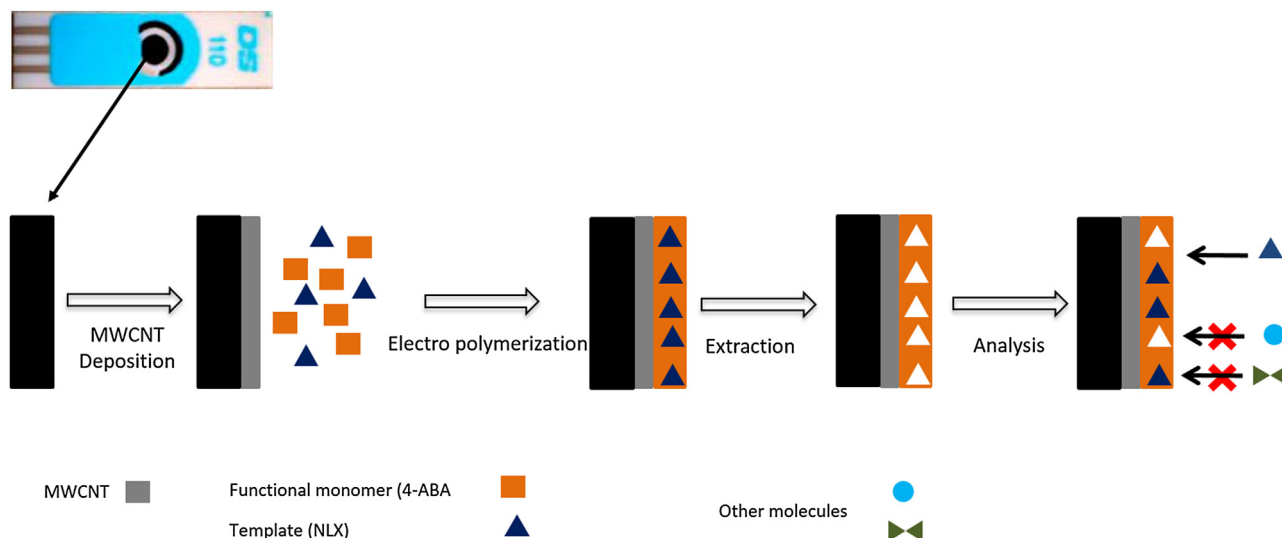


Fig. 1. Schematic illustration of the preparation of the MIP/MWCNT/SPCE electrode.

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