



Computational design and development of a novel voltammetric sensor for minoxidil detection based on electropolymerized molecularly imprinted polymer



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ARTICLE INFO

Article history:

Received 28 September 2014

Received in revised form 10 December 2014

Accepted 15 December 2014

Available online 6 January 2015

Keywords:

Molecular imprinted polymer

Electropolymerization

Computational design

Silver nanoparticles

ABSTRACT

A novel electrochemical sensor based on molecularly imprinted polymer (MIP) with sensitive and selective binding sites for minoxidil (MX) were developed. The MIP film was cast on the glassy carbon electrode by electrochemical polymerization in a solution containing ternary monomers and MX as a template via cyclic voltammetry scans. The coated polymer was further modified by Ag nanoparticles (NPs). The selection of the suitable functional monomer(s) was based on the interaction between different monomers and template using the density functional theory (DFT). The resulted modified electrode was characterized by cyclic voltammetry (CV), scanning electron microscopic (SEM) and electrochemical impedance spectroscopy (EIS). Under the optimum conditions, the oxidation peak current was proportional to MX concentration over the range of 0.03–500 μM . The detection limit (LOD) was found to be 0.01 μM . This sensor was successfully applied for the determination of MX in real samples.

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1. Introduction

Minoxidil (2,4-diamino-6-piperidinopyrimidine-3-oxide, MX) is a vasodilator that relaxes (widens) the blood vessels and improves the blood flow, and it is applied for the treatment of refractory hypertension patients [1]. The excessive oral administration of this drug to the patients should cause liquid retention and hirsutism [2]. MX has a new application in dermatology, especially in the treatment of androgenic alopecia [2–5]. Several methods such as liquid chromatography [6,7], photometric titrations [8], UV–vis spectrophotometry [9], flow injection with photometric [10] and polarography plus spectrophotometry [11] have been reported for determination of MX. The electroanalytical methods as alternative methods have some important advantages, including speed, high sensitivity, relative simplicity and low costs. In recent years, chemically modified electrodes have attracted more interest due to their potential applications in the electroanalytical chemistry [12–16]. Literature survey shows a few electrochemical reports for the determination of MX, which are based on its reduction or oxidation [1,17–19]. In order to increase the selectivity of the sensor even in the presence of compounds with structures and functionality similar to that of the target compound (template),

different modifiers such as molecularly imprinted polymers (MIPs) have been used [20–22]. MIPs are cross-linked macromolecules bearing “tailor-made” binding sites for target molecules and are prepared by the complexation in the solution of a template with functional monomers, through either covalent or non-covalent bonds, followed by polymerization with an excess of cross-linker to form a highly cross-linked polymer network. Upon removal of the template molecule from the polymer network, the specific recognition sites that are complementary to the template in terms of their size, shape, and functionality are exposed [23,24]. This approach, which is most commonly used to prepare polymer has some limitations such as slow mass transfer, incomplete template removal, and heterogeneous distribution of the binding sites and decreases the adherence to a transducer [25–27]. The electrochemical polymerization approach is one of the efficient ways to solve these limitations by generating a rigid, uniform and compact molecularly imprinted film with controlled thickness, which has improved sensitivity with good adherence to a transducer of any size and shape [28,29].

However, in order to avoid the synthesis of the MIPs with trial and error, the computational methods are used as an alternative approach for the rational design of MIPs [30–32]. In this regards the density functional theory (DFT) method is widely used to select functional monomers by calculating the energy difference (ΔE) [33–35].

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Meanwhile, metal nanoparticles (NPs) can play an important role in improving the sensor performance, due to their large specific surface areas, excellent conductivities, small particle size and good electrical properties [36–38]. Therefore, in the present study, silver NPs (AgNPs) are chosen to amplify the electrochemical response due to their high electrical conductivity and strong stability in an aqueous environment.

In this work, a MX sensor based on the polymer of o-phenylenediamine-co-gallic acid-co-p-aminobenzoic acid functional monomers were constructed by electropolymerization and subsequently, electrochemically deposition of Ag NPs for the first time. DFT-based computational approach was used as the rational design of MIPs for MX as template molecule. The experimental parameters that affect the performance of the imprinted sensor were investigated and optimized. The detection procedure is based on the oxidation of MX after its selective extraction in the modified electrode using square wave voltammetry. The developed sensor has been successfully applied to determine MX in the real samples.

2. Experimental

2.1. Reagents and apparatuses

Voltammetric measurements were carried out with an Autolab (Eco Chemie B. V., Netherlands) PGSTAT30 potentiostat/galvanostat equipped with a USB electrochemical interface and driven by a NOVA 1.8 software package in conjunction with a three-electrode system. A three-electrode cell system consisted of unmodified and modified glassy carbon electrode (GCE) as working electrode, Ag/AgCl and platinum wire as a reference and counter electrodes. All the measurements were carried out at room temperature. A Metrohm pH-meter (model 691, UK) was also applied for pH measurements. Scanning electron microscopy (SEM) images were obtained with a field emission gun scanning electron microscope (Philips XL 30, USA).

O-phenylenediamine (OP), gallic acid (GA) and p-aminobenzoic acid (ABA) were purchased from Sigma–Aldrich (Munich, Germany). A 1.0 mM stock solution of MX (a), mezalamine (b), amoxicillin (c) and phenylephrine (d) were prepared in water. MX, mezalamine, amoxicillin and phenylephrine were obtained from Merck (Darmstadt, Germany) and their chemical structures are shown in Scheme 1. All the other chemicals were from the analytical grade and were purchased from Merck (Darmstadt, Germany). All the solutions were stored at 4 °C in protection against the light. Ethanol–water solution (2:1, v/v) was used to extract the template from the MIP matrix. Phosphate buffered solutions (PBS) (0.01 M) at various pH values were prepared by 0.01 M H₃PO₄, 0.01 M KH₂

PO₄ and 0.01 M K₂HPO₄ and then adjusted the pH with 0.2 M HCl or 0.2 M NaOH.

2.2. Computational approach

DFT was used as implemented in the Firefly quantum chemistry package to calculate the structures of the complex forming between MX and individual, binary or ternary mixtures of OP, GA and ABA monomers [39]. The B3LYP hybrid DFT method that involved 20% of exact exchange and included three semi-empirical parameters was employed in this work [40,41]. The 6-31G (d,p) basis sets were used for DFT calculation [42]. All the structures were plotted with Avogadro software. The binding energy of MX–monomer(s) complex, ΔE , were calculated according to the following equation:

$$\Delta E = E(\text{complex}) - E(\text{MX}) - \sum_{i=1}^N E(\text{monomer}_i) \quad (1)$$

where N , $E(\text{MX})$, $E(\text{monomer}_i)$ are number of monomer, the energy of MX and the energy of monomer respectively. Due to artificial strengthening of the intermolecular interaction, the basis set super position error (BSSE) was used for accurate calculation of the weakly bound cluster between monomers and monomers–template [43,44]. The BSSE calculation for designing the suitable functional monomers in MIP preparation has been previously reported [45].

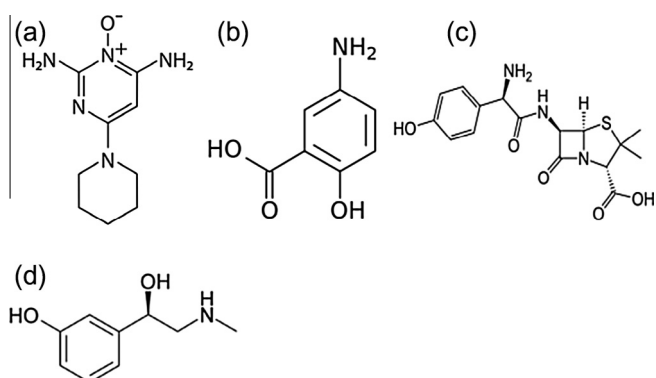
The extended counterpoise correction (CP) software was used for investigation of the interactions between monomers (donated as A, B and C) and template (D) according to the following equation [46]:

$$\Delta E_{\text{int}}^{\text{CP}}(\text{ABCD}) = E_{\text{ABCD}}^{\text{ABCD}}(\text{ABCD}) - E_A^{\text{ABCD}}(A) - E_B^{\text{ABCD}}(B) - E_C^{\text{ABCD}}(C) - E_D^{\text{ABCD}}(D) \quad (2)$$

where $\Delta E_{\text{int}}^{\text{CP}}(\text{ABCD})$, $E_{\text{ABCD}}^{\text{ABCD}}(\text{ABCD})$, $E_A^{\text{ABCD}}(A)$, $E_B^{\text{ABCD}}(B)$, $E_C^{\text{ABCD}}(C)$, $E_D^{\text{ABCD}}(D)$ are counterpoise interaction between the four components, the energy of the component ABCD, A, B, C. The solute dipole moment induces a dipole moment with the opposite direction in the surrounding medium (solvent) and its result to change the charge distribution in the solvent [40–43]. The polarizable continuum model (PCM) has been used for the DFT calculation of the stabilization energy of MX and its interaction with all the individuals and or the mixtures of the functional monomers (OP, GA, ABA) in water as a solvent [47].

2.3. Preparation of the MIP modified electrode

The general procedure to prepare imprinted polymer was as the previous report [48]. The surface of the bare GCE was polished with 0.3 and 0.05 μm alumina–water slurry and ultrasonicated in HNO₃, ethanol, and doubly distilled water for 10 min. Then cyclic voltammetry was performed with the potential range from –0.5 to 2.0 V in 0.5 M H₂SO₄ at 100 mV s^{–1} until a stable cyclic voltammogram was obtained. The GC electrode modified with MIP was prepared by electropolymerization of ternary monomer mixture (OP–GA–ABA) in the presence of MX as a template using cyclic voltammetry. Fifteen consecutive cyclic scans in the potential range of –0.4 and +0.8 V at a scan rate of 50 mV s^{–1} in a 10 mL of 0.01 M phosphate buffer solution (PBS, pH = 3) containing 0.2 M KCl, 40 μmol OP, 20 μmol GA, 20 μmol ABA and 10 μmol MX were used for the construction of the MX–MIP/GC electrode. For the comparison, the reference non-imprinted polymer/GCE (NIP/GCE) was constructed using the same procedure in the absence of template molecule. The electrodes were washed with distilled water for several times and then immersed in a solution containing NaNO₃ (0.1 M) and AgNO₃ (2.5 mM). AgNPs were deposited on the



Scheme 1. Structure of compounds which were examined for Ag NPs/MIP/GCE selectivity. (a) MX, (b) mezalamine, (c) amoxicillin and (d) phenylephrine.

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