Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Reactive & Functional Polymers 63 (2005) 171–176
REACTIVE & FUNCTIONAL POLYMERS
www.elsevier.com/locate/react

Interaction of ochratoxin A with molecularly imprinted polypyrrole film on surface plasmon resonance sensor

Jorn C.C. Yu, Edward P.C. Lai *

Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ont., Canada K1S 5B6

Received 23 June 2004; received in revised form 4 March 2005; accepted 4 March 2005
Available online 29 April 2005

Abstract

A molecularly imprinted polypyrrole (MIPPy) film was synthesized on the Spreeta sensor, a miniaturized surface plasmon resonance device, for detection of ochratoxin A (OTA). The MIPPy was electrochemically polymerized on the sensor surface from a solution of pyrrole and OTA in ethanol/water (1:9 v/v). The film growth was monitored in situ by an increasing SPR angle. Binding properties of the MIPPy film were investigated by loading OTA standard solutions into the integrated 20-μL flow cell. After 300 s, nonlinear regression was used to determine the maximum binding signal (Δ_{300}). Spreeta results showed that Δ_{300} was measurable for OTA concentrations down to 0.05 ppm. By pulsed elution, 1% acetic acid in methanol/water (1:9 v/v) was found to be efficient for regeneration of the MIPPy film surface. Interference by the matrices of wheat and wine extracts was evaluated. No significant binding of the wheat extract with MIPPy was observed when acetonitrile/water (1:1 v/v) was used as the mobile phase.

Keywords: Surface plasmon resonance; Polypyrrole; Molecularly imprinted polymer; Ochratoxin A; Spreeta

1. Introduction

Molecularly imprinted polymers (MIPs) have been considered to be the man-made material which can provide high affinity to specific target molecules. The concept underlying molecular imprinting is self-assembly of functional monomers around the template molecule, followed by polymerization in the presence of excess cross-linkers to form a solid material. Upon removal of the template, recognition cavities are created that are complementary in both shape and functionality to the original template. The binding of functional monomers to the template can be achieved by non-covalent interactions, thereby allowing considerable flexibility in the choice of functional monomers for imprinting

* Corresponding author. Tel.: +1 613 520 2600x3835; fax: +1 613 520 2569.
E-mail address: edward_lai@carleton.ca (E.P.C. Lai).

1381-5148/$ - see front matter
doi:10.1016/j.reactfunctpolym.2005.03.001

various types of templates [1]. MIPs have been developed for a variety of applications including chromatography, enzymatic catalysis, solid-phase extraction, and sensor technology [2]. The molecular imprinting technique has been applied in quartz crystal microbalance (QCM) [3] and capillary electrochromatography column [4], to serve as the sensing element and the stationary phase, respectively. In the field of modern analytical chemistry, sensors with a high capacity for transducing chemical signals are highly desirable [5]. However, there are challenges associated with the development of MIP-based sensors, such as the paucity of a general procedure for preparing MIP films, difficulty in integrating them with a transducer, and the lack of sensitivity in transforming the binding event into measurable signals [6].

Surface plasmon resonance (SPR) sensors are useful for measuring thin film thicknesses (with a resolution at the angstrom-to-nanometer level) and detecting molecular interactions [7,8]. Previously, Lai et al. [9] prepared a MIP overlayer (from methacrylic acid and ethylene glycol dimethacrylate) for use as the sensing element in SPR detection of theophylline, caffeine, and xanthine. Kugimiya and Takeuchi [10] synthesized a MIP on a SPR device by co-polymerizing *N*,*N*,*N*-trimethylaminoethyl methacrylate, 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate in the presence of *p*-vinylbenzeneboronic acid ester for the detection of sialic acid. Li et al. [11] fabricated a MIP with L-phenylalanine ethyl ester and used SPR for monitoring the adsorption and elution processes in situ. Taniwaki et al. [12] demonstrated that SPR was a convenient and facile method to detect molecular recognition interactions.

Polypyrrole (PPy) is one of the most promising materials for multifunctionalized applications. The preparation, characterization, properties and applications of PPy has been reviewed by Wang et al. [13]. According to the synthetic methods, various parameters (such as doping anions, additives and oxidants) have different effects on the PPy properties. For example, PPy doped with small-sized anions act as anion exchange materials [14]. Minehan et al. [15] reported the use of PPy for binding DNA. They found that the positively charged surface largely enhanced the adsorption of negatively charged colloidal particles through electrostatic interaction to form surface complexes. Electrochemical polymerization results in thin PPy films on the working electrode surface [16,17], which would be suitable for SPR sensor applications. Guedon et al. [18] demonstrated that the PPy film could be electrospotted on gold surfaces and that SPR imaging allowed real-time measurements on several spots at a time.

Recently, the possibility of inducing selectivity by the presence of a template during polymerization was tested by Blanco-Lopez et al. [19] with several non-cross-linked electrogenerated polymers such as PPy. The objective of our present work was to integrate molecularly imprinted polypyrrole (MIPPy) films with a miniaturized SPReeta device for OTA detection in wheat and wine extracts. Each MIPPy film was prepared electrochemically on the Spreeta gold surface from a solution of pyrrole and OTA in ethanol/water (1:9 v/v). This integrated preparation provided a simple and rapid way to synthesize a sensing element with targeted selectivity. The OTA binding property of each MIPPy film was directly monitored by SPR, and pulsed elution was developed for regeneration of the MIPPy film. Interference by the matrices of wheat and wine extracts was evaluated and minimized.

2. Experimental

2.1. Materials

Ochratoxin A (OTA) and pyrrole (Py) were purchased from Sigma–Aldrich (Mississauga, Ont.). Acetonitrile, methanol, and ethanol were all HPLC-grade obtained from Caledon (Georgetown, Ont.). Acetic acid was purchased from Fisher Scientific (Fair Lawn, NJ). 18-MΩcm distilled deionized water (DDW) was supplied from a Millipore Milli-Q water system (Bedford, MD).

2.2. Instrumentation

The SPReeta evaluation module (SPR-EVM-BT) was purchased from Nomadics (Stillwater,