Sensors and Actuators B 200 (2014) 25–30

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Short communication

Gravimetric detection of theophylline on pore-structured molecularly imprinted conducting polymer

Jong-Min Kim[a], Un-Hak Lee[a], Sang-Mok Chang[a], Jin Young Park[b,*]

[a] Department of Chemical Engineering, 37 Nakdong-daero, 550 beon-gil, Saha-gu, Busan 604-714, Republic of Korea
[b] Department of Polymer Sciences & Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu 702-701, Republic of Korea

ARTICLE INFO

Article history:
Received 2 January 2014
Received in revised form 3 April 2014
Accepted 11 April 2014
Available online 24 April 2014

Keywords:
Molecularly imprinted conducting polymer (MICP)
Colloidal lithography
Polystyrene colloidal beads
Electropolymerization
Theophylline
Polypyrrole

ABSTRACT

A novel molecularly imprinted conducting polymer (MICP) system with porous thin films of electropolymerized polypyrrole (Ppy) derivatives was successfully developed to detect a specific target molecule (e.g. theophylline). The porous MICP films grown on gold pore arrays through cyclic voltammetry showed increased sensing response in detecting theophylline compared to a conventional planar MICP film due to its improved sensing capacity.

1. Introduction

Molecularly imprinted polymers (MIPs) have highly interesting potential in developing sensing systems for recognizing a selective binding site for a specific molecule [1,2]. The recognition site mimics the binding site of a template, involving an interaction mechanism based on creating a cavity with the imprinting of the template. Therefore, these MIPs have extensively been used for the detection of various specific molecules such as amino acids [3,4], pesticides [5], proteins [6], etc. In particular, molecularly imprinted conducting polymers (MICPs) [7] are very attractive in generating nanometer scale structures for a specific recognition and increasing the cavities for rebinding templates. Various electroactive molecules have been used for a template by electrochemically imprinting techniques [8–10]. Commonly several monomers such as pyrrole [11,12], thiophene [13], 3,4-ethylenedioxythiophene (EDOT) [14,15], and carbazole [16] have been used to develop MICP systems.

Polypyrrole (Ppy) has been extensively used in various applications, such as electronic devices/chemical sensors and polymer matrix container for proteins [17,18]. As MICP sensors, Ppy-MICP has been developed to recognize various templates [19–21]. For example, Öpik et al. [22] studied the overoxidized polypyrrole film templated L-aspartic acid (L-Asp) for enantioselective detection. In potentiodynamic conditions and strongly acidic media the MICP film showed significantly higher sensitivity for L-Asp compared to D-Asp. Furthermore, Ppy-MICP sensing systems, prepared by cyclic voltammetry (CV), exhibited a high selectivity and sensitivity toward a template molecule (paracetamol) [23].

Recently, various micro- and nano-sized MIPs was studied to imprint specific molecules for analytical applications [24]. For example, the formation of MIP microstructures via a templating process using soft lithography was achieved as a novel approach to MIP systems [25,26], and 2,4-dichlorophenoxyacetic acid (2,4-D) molecular recognition in electrospun polymer nanofibers was developed [27]. Furthermore, Ppy-MICP nanonecklaces were studied through a two-step oxidative polymerization process [28]. Similarly, pyrrole nanowire MIPs were also prepared by electrochemical polymerization to recognize chiral amino acids (enantiomeric camphorsulfonic acid; D- or L-CSA) [29]. However, even though many efforts have been made, in my knowledge, the studies on the nano-/micro-structuring of a conductive surface for MICP electrosynthesis to develop improved sensing systems have not yet been done. In this regard, we considered novel MICP sensing nanoplatform candidates adopting a morphology-controlled fabrication method via colloidal lithography. Herein we attempted

---

* Corresponding author. Tel.: +82 53 950 5624; fax: +82 53 950 6623.
E-mail address: jinpark@knu.ac.kr (J.Y. Park).

http://dx.doi.org/10.1016/j.snb.2014.04.042
0925-4005/© 2014 Elsevier B.V. All rights reserved.

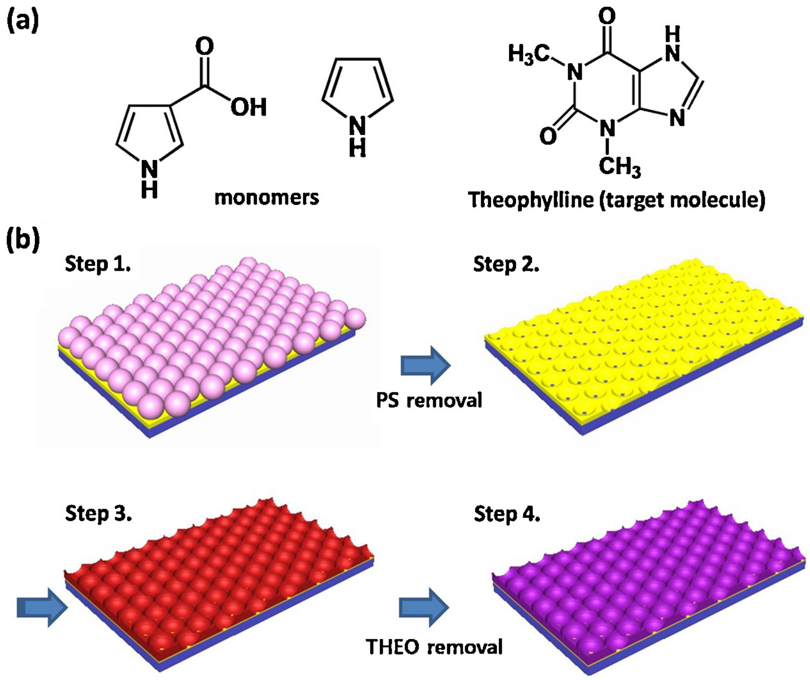

Fig. 1. (a) Chemical structures of monomers and theophylline (THEO) used and (b) schematic illustration of the fabrication process of poly(py-*co*-py-3-carbox) MICP films made by using colloidal lithography and electrochemical methods (step 1: gold electrochemical deposition on PS colloidal array, step 2: gold pore array after the removal of the colloids, step 3: a porous poly(py-*co*-py-3-carbox) MICP film made by electropolymerization and step 4: removal of THEO on the *p*-MICP film).

to electrosynthesize poly(pyrrole-*co*-pyrrole-3-carboxylic acid) [as denoted by poly(py-*co*-py-3-carbox)] films as a MICP matrix on various porous gold arrays (conductive electrodes), electrochemically obtained from polystyrene (PS) colloidal monolayers. Compared to a planar MICP film, this porous structure should allow binding sites to be increased, resulting in increased sensing response for theophylline (THEO, dimethylxanthine) which is a drug used in therapy for respiratory diseases.

2. Experimental

2.1. Materials

Chloroauric acid ($HAuCl_4$), ethylenediaminetetraacetic acid (EDTA), sodium sulfite (Na_2SO_3), and dipotassium phosphate (K_2HPO_4) were purchased from Sigma–Aldrich for the electrosynthesis of porous gold films. Pyrrole ($M_w = 67.09$, Sigma–Aldrich) and pyrrole-3-carboxylic acid ($M_w = 111.10$, Alfa Aesar) were used as monomers for a molecularly imprinted conducting polymer matrix. Lithium perchlorate ($LiClO_4$, $M_w = 106.39$) purchased from Acros Organics was used as electrolyte for electropolymerization. PS colloids (500, 750, and 1000 nm) were obtained from Alfa Aesar. In molecularly imprinted system, theophylline ($M_w = 180.16$, Sigma–Aldrich) was used as a target molecule.

2.2. PS colloidal array

Two-dimensional (2-D) colloidal arrays with a hexagonal structure were prepared following several steps reported elsewhere in the literatures [30–33]. To prepare PS colloidal arrays, glass substrates were first rinsed with H_2O and acetone. After dried with nitrogen gas (N_2), they were immersed in piranha solution (H_2SO_4:$H_2O_2 = 3:1$, v/v) for 40 min (CAUTION: strong oxidizing solution). A PS stock solution (100 μl, 80 μl, and 80 μl for 500, 750, and 1000 nm PS colloidal suspension) was spread out on the prepared glass using micropipette. Then, using a spin-coater (Mikasa Opticoat, MS-A150), specific spinning speed and time were set for each colloid bead solution (400 rpm and 5 min for 500 nm, 300 rpm and 5 min for 750 nm, and 300 rpm and 7 min for 1000 nm) to spread colloidal suspension. After spin-coating, the glass substrate with colloid array did not have a highly packed structure. To overcome this negative phenomenon, the PS colloidal array on the substrate was transferred on water surface in a plastic Petri-dish where SDS solution of 200–300 μl was pre-spread using a micropipette. In case, more SDS solution needs to be dropped on water surface for a highly dense monolayer. Finally, the floating PS colloidal array in solid state was scooped on 9 MHz AT-cut quartz crystal microbalance (QCM) substrates and dried for a day to remove moisture.

2.3. Gold pore arrays

Potentiostatic electrodeposition was performed to grow gold particles from the interstices among the PS colloids in the monolayer. Using a potentiostat (CH Instruments, Inc.), a voltage of −0.7 V (vs. Ag/AgCl) was applied in an aqueous electrolyte [$HAuCl_4$ (12 gL^{-1}), EDTA (5 gL^{-1}), Na_2SO_3 (160 gL^{-1}), and K_2HPO_4 (30 gL^{-1})] according to the literature [34]. After the gold growth, the PS collodial arrays were removed by thoroughly rinsing with toluene. The porous structures and thickness on the gold films were controlled upon the electrodeposition time.

2.4. Molecularly imprinted conducting polymer (MICP)

A copolymeric matrix [poly(py-*co*-py-3-carbox)] were electropolymerized in an aqueous solution of 0.1 M $LiClO_4$, 0.03 M Py-COOH, and 8 mM pyrrole in the presence or absence of 15 mM theophylline. To grow MICPs, cyclic voltammetry (CV) was performed in a three-cell electrochemical setup, connected with potentiostat (Princeton Applied Research, model 263A). A quartz crystal substrate with PS colloidal array was used as a working electrode. A platinum wire and saturated calomel electrode (SCE) were a counter and a reference electrode, respectively. The grown film was controlled by the number of sweep cycles (0–1.2 V vs. SCE at a