Sensors and Actuators B 216 (2015) 476–481

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Lithographically patterned molecularly imprinted polymer for gravimetric detection of trace atrazine

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ARTICLE INFO

Article history:
Received 22 January 2015
Received in revised form 17 April 2015
Accepted 17 April 2015
Available online 30 April 2015

Keywords:
Molecularly imprinted polymer (MIP)
Soft lithography
UV-initiated polymerization
Atrazine
Herbicide
Poly(MAA-EGDMA)

ABSTRACT

In this paper, we examined a novel molecularly imprinted polymer (MIP) patterned matrix, consisting of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) as functional and cross-linking monomers, respectively, for detection of trace atrazine in an aqueous solution. A solvent assisted soft lithography and UV-initiated polymerization were used to develop striped poly(MAA-EGDMA) patterns. In comparison to a planar MIP film ($\Delta f_{p\text{-}MIP} = -158$ Hz), the striped patterns showed faster sensing response ($\Delta f_{s\text{-}MIP} = -269$ Hz) for the 30 min detection period due to the relatively increased binding sites generated from the MIP stripes. Furthermore, the sensitivity of the MIP sensor was found to be -9.98 Hz $(\mu M)^{-1}$ via gravimetric quartz crystal microbalance (QCM) measurements and the selectivity of the MIP stripes was evaluated through sensing characteristics of other herbicides. Thus, a control of binding sites via this lithographic technique could contribute to the development of efficient MIP sensing platforms.

1. Introduction

Atrazine is one of common triazine class herbicides that have been widely used on crops, golf courses and residential lawns for several decades because of effectively reduction of crop losses and removal of weed. It was the most commonly detected in well water, groundwater, and drinking water contaminates. Short-/long-term exposure to atrazine causes endocrine disruption, neuropathy, and cancer in humans [1]. Therefore, actions have been taken to control this herbicide and require measuring amounts in drinking water. For detection and analysis of herbicides at trace levels, instead of gas and liquid chromatography [2], molecular imprinting technique as alternative analytical tool has been recently attractive due to less time-consuming and low cost.

Molecularly imprinted polymers (MIPs) have been extensively attractive in various research fields such as bio-/chemical sensors, chromatography, bioanalysis (in vitro diagnostics, therapeutics) and separation science due to a recognition process of a specific molecule on selective binding sites [3–6]. In general, MIP systems can be designed through electrochemically or chemically synthetic approaches [7–11], associated with non-covalent bonds (such as hydrogen bonding, dipole–dipole, and ionic interaction) between templates and MIP matrices. The proper use of physical or chemical interactions makes it possible to easily prepare nanometer-scale structured MIPs for a specific recognition and to do electrochemical [12,13], optical [14], or gravimetric [15–17] analysis for template sensing. Many research groups have studied on atrazine sensing MIP systems using various methodologies, such as porous membranes [18,19] and nanostructures [core–shell [20] and nanoparticles [21]]. To fabricate MIPs for atrazine detection, methacrylic acid (MAA) [or methyl methacrylate (MMA)], ethylene glycol dimethacrylate (EGDMA), and 2,2′-azobis(2-isobutyronitrile) (AIBN) have been used for two common methods in the synthesis of imprinted polymers, i.e. UV(or IR)-initiated [22,23] and thermal polymerization [24,25]. However, the UV-initiated polymerization reaction has been mostly performed due to relatively short-period reaction process.

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http://dx.doi.org/10.1016/j.snb.2015.04.079
0925-4005/

Related to MIP nano-/micro-structuring on the substrates, molecularly imprinted photonic polymers (MIPP) with 3D-ordered interconnected macroporous structure were recently used for colorimetric detection [14]. This system allows rapid and ultra-sensitive detection of the trace atrazine template. Similarly, our group has developed two porous MIP systems for detection of theophylline using colloidal lithography and electropolymerization [26,27]. These novel sensors provided highly increased surface sensing binding sites depending on porous structures and dimensions of porous electrodes or MIP films. Furthermore, by employing micromolding in capillaries (MIMIC) and a soft poly(dimethylsiloxane) (PDMS) stamp, isolated MIP micromonoliths were fabricated to detect 2,4-dichlorophenoxyacetic (2,4-D) acid herbicide [28]. However, several limits arise in this MIP sensing systems. Firstly, to use MIMIC process, the micro-scale cross-sectional area of a channel (a few μm^2) needs to be used so that fluids having low viscosity (<300 cP) flow into the channels [29]. In addition, empty spaces among micromonoliths formed on planar substrates do not contribute to sensing responses on MIP systems.

In this study, submicron-patterned MIP systems consisting of poly(MAA-EGDMA) as the recognition platform of trace atrazine is developed using soft lithography and UV-initiated polymerization. This patterned MIP matrix would provide more nanocavities due to increased surface areas formed from patterns and a thin residual layer among patterns, compared to a planar MIP system. The relatively increased surface area is favorable for the rapid transport of atrazine in MIP films and allows selective recognition of atrazine over the nanocavites distributed in a thin polymer surface. Also, the detection of trace atrazine with a broad concentration range varying from 10^{-6} M to 10^{-10} M in a mixture solution is achieved and selective detection is examined by investigating the sensing responses with other herbicides.

2. Materials and methods

2.1. Materials

To make a MIP matrix, MAA (Daejung Chemicals & Metals Co.), EGDMA (Sigma-Aldrich Co.), and 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine (atrazine, Sigma-Aldrich Co.) were used as monomer, cross-linker, and template, respectively. AIBN (Daejung Chemicals & Metals Co.) was used as photo-initiator. Dimethylformamide (DMF) as solvent was obtained from Tokyo Chemical Industry Co. Amteryn, prometryn (Sigma-Aldrich Co.), and 2,4-D (TOKYO Chemical Industry Co.) as other herbicides were used for selectivity test. All other solvents with analytical reagent grade were used without any purification.

2.2. Patterned PDMS mold

Firstly, after violently mixing silicone elastomer and curing agent (10:1 weight ratio, Sylgard 184, Dow Corning Co.) air bubbles generated were removed via vacuum degassing method and the mixture was carefully poured onto a master mold with line patterns (periodicity: 1400 nm, width: 1100 nm, height: 150 nm, see Supporting information Fig. S1) placed in a plastic petri dish. After thermal curing at 70 °C for 2–3 h, the patterned PDMS was successfully replicated and cut to a specific cut size ($20 \times 20\ mm^2$). Then, they were stored in a clean petri dish before use.

2.3. MIP patterning

MAA (4 mM), atrazine (1 mM), EGDMA (20 mM) were dissolved in DMF solution (100 μl) and sonicated for 15–20 min (Fig. 1). AIBN

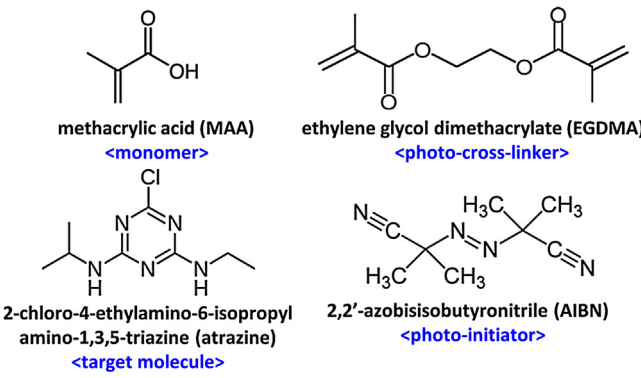

Fig. 1. Chemical structures used in this study.

(1 mM) was then added in the mixture solution and the solution in the vial was purged with nitrogen gas (N_2) for 10 min. As a pre-curing step, the imprinting solution was irradiated under UV lamp (370 nm, 36 W) for a short period of time (40–50 s) to make it slightly viscous for a conveniently subsequent process (i.e. PDMS stamping in lithographic process). Also, a mixture solution without template molecules was prepared in a similar manner to make non-imprinted polymer (NIP) film.

For line-patterned MIP films, glass substrates were firstly sonicated with acetone, ethanol, and deionized (DI) water for 5 min and then immersed in piranha solution (H_2SO_4:H_2O_2 = 3:1, v/v) for 40–50 min (CAUTION: strong oxidizing solution). After rinsing with DI water, the substrates were stored in a glass jar containing DI water prior to use. As shown in experimental scheme (Fig. 2), a fabrication process of MIP patterned films is as follows: an imprinting solution of 5 μl was carefully dropped on the substrate, the patterned PDMS mold was carefully placed on the droplet of solution, and then the certain pressure was induced on the mold to retain enough physical contact between the PDMS and substrate during the replication process. UV-initiated polymerization was then performed for 7–10 min. After demolding, the patterned MIP films were dried at 60 °C for 2–3 h to remove the residual solvent and complete polymerization. Continuously, MIP films were immersed into a mixture solution of DI water, methanol, and acetic acid (1/4/1, v/v/v) for 15 min to remove the atrazine template through a process of breaking the hydrogen bonding between carboxylic group on MAA monomers and amino group on atrazine templates and finally rinsed with methanol [28]. In order to perform quantitative analysis in a rebinding process, patterned MIP films were prepared on 9 MHz gold-coated AT-cut quartz crystals (active gold area: 0.196 cm^2) via the same lithographic method. Related to the atrazine rebind process, the resonant frequency was *in-situ* monitored in 10^{-6} M atrazine-contained mixture solutions (H_2O:C_2H_5OH = 1:1, v:v) with various concentrations for 30 min using QCA 922 analytical instrument.

2.4. Characteristics

Atomic force microscopy (AFM, Digital Instruments, Nanoscope IV) with commercially available tapping mode tips (Nano World, Al-coating silicon, f_0: 320 kHz) was used to investigate surface topography and dimension of porous structures. The AFM measurements were carried out with a piezoscanner capable of scanning an area of $100 \times 100\ \mu m^2$ at room temperature and a scan rate of 1.0 Hz. All images (AFM topography, tapping mode) were flattened, filtered, and analyzed by using SPIP software (Scanning Probe Image Processor, Imagemet.com). Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used to investigate the surface topographies of patterned MIP films. Energy-dispersive