Sensors and Actuators B 258 (2018) 228–237

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Research paper

Selective and sensitive sensors based on molecularly imprinted poly(vinylidene fluoride) for determination of pesticides and chemical threat agent simulants

Xuan Hao Lin[a], Shalen Xue Ling Aik[a], Jacelyn Angkasa[a], Qihui Le[a], Kah Sing Chooi[a], Sam Fong Yau Li[a,b,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[b] NUS Environmental Research Institute (NERI), #02-01, T-Lab Building (TL), 5A Engineering Drive 1, Singapore 117411, Singapore

ARTICLE INFO

Article history:
Received 6 August 2017
Received in revised form 18 October 2017
Accepted 15 November 2017
Available online 23 November 2017

Keywords:
Sensor
Polymer
Poly(vinylidene fluoride)
Methyl parathion
Molecular imprinting

ABSTRACT

Molecular recognition in molecularly imprinted polymers (MIPs) is attributed to complementary binding sites with same or similar size, shape, and functionality to imprint molecules. A new selective and sensitive sensor based on molecularly imprinted poly(vinylidene fluoride) (PVDF) polymer for the detection of methyl parathion (MP), a ubiquitous highly hydrophobic pesticide that is commonly used as a simulant of chemical threat agents. The PVDF-based sensor was prepared using the molecular imprinting method with a pre-polymerized PVDF instead of traditional in-situ or post- polymerized ones to avoid harsh and tedious polymerization conditions. In addition to size and shape of the imprinted cavities, the developed PVDF-based sensors could exhibit high selectivity and sensitivity mainly due to dipole-dipole interaction, hydrophobic interaction and van der Waals interactions with the template MP molecules. The results show that the prepared PVDF-based sensor indeed showed high selectivity towards MP against other pesticides such as diethyl phosphoramidate, dicrotophos, 2,4,5-trichlorophenoxyacetic acid, and terephthalic acid achieving a limit of detection (LOD) of 68.0 nM and a limit of quantitation (LOQ) of 226.8 nM using quartz crystal microbalance as sensor platform. The specificity and selectivity of the prepared MIP were further verified with detection of the analyte in spiked vegetable samples.

1. Introduction

Molecularly Imprinted Polymers (MIPs) have been widely applied in various applications, i.e. plastic antibodies [1,2], drug delivery [3,4], separation and purification [5], and sensors for various chemical and biochemical analyte molecules [6–10]. MIP consists of polymers with molecular recognizing cavities imprinted from the imprint (template) molecules. Monomers and template molecules interact with each other through covalent or non-covalent bonds. Monomers are polymerized so that templates are embedded in polymer matrix. Subsequently templates are removed leaving molecularly imprinted cavities in polymer. Molecular recognition is attributed to complementary binding sites with the same size, shape, and functionality as those of templates.

Shi et al. [10] reported surface imprinted fluoropolymer for the recognition of proteins. Protein template molecules were deposited onto freshly peeled mica, followed by adsorption of disaccharides and subsequent radio-frequency glow-discharge plasma deposition of polymer using C_3F_6. Then the polymer was attached to a glass support using epoxy resin and oven-cured. Subsequently mica was peeled off and the surface was cleaned with oxidative alkaline solution to remove protein residuals, leaving the protein-recognition sites on the surface. It is worthy to highlight that the imprint proteins are not directly imprinted to polymer but through a "sugar shell", which interacts well with template proteins during dehydration and also inhibits drying-induced denaturation or plasma-induced degradation. Ouyang et al. [9] developed an o-phenylenediamine and dopamine based copolymer electrochemically imprinted with enantiomer L- or D- glutamic acid. The enantiometric selectivity coefficients for L- and D- glutamic acid imprinted copolymer against their respective enantiomers are as high as 24 and 15, respectively. Zhou et al. [7] developed polydopamine-based MIP sensor for the detec-

* Corresponding author at: Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543 Singapore.
E-mail address: chmlifys@nus.edu.sg (S.F.Y. Li).

https://doi.org/10.1016/j.snb.2017.11.070
0925-4005/

tion of domic acid. The main interactions between polydopamine and template molecules, i.e. 1,3,5-pentenetricarboxilic acid, are hydrogen-bonding. The template molecules are similar to the analyte molecules, i.e. domic acid, but not the same. The prepared sensor shows good selectivity towards domic acid against interfering molecules p-phthalic acid and o-phthalic acid. Katz and Davis [11] prepared molecularly imprinted bulk microporous silica (non-polymer) using template molecules carrying up to three 3-aminopropyltriethoxysilane side groups, which are eventually attached to the micropores of silica while template molecules are removed through chemical reactions. D'Souza et al. [12] demonstrated feasibility of imprinting calcite crystal (non-molecules) onto a polymer of metharylamidohexanoic acid cross-linked with divinylbenzene. The imprinted polymer is able to promote nucleation of calcite. Besides polymers and inorganic materials, other materials may also be used for molecular imprinting. Zimmerman et al. [6] synthesized monomolecule-imprinted dendrimer where the template molecules are covalently bonded to the dendrimer and their removal involves cleavage of covalent bonds through hydrolysis.

Traditional MIP preparation process is usually harsh and tedious. Kubo et al. [13] reported a MIP for methotrexate, an anticancer drug. They synthesized the MIP through thermal polymerization at 40 °C for 24 h in dimethylsulfoxide (DMSO) using mathacrylic acid (MAA), sodium p-styrenesulfonate (SS), 4-vinylpyridine (4Vp), (vinylbenzyl) trimethylammonium chloride (VBTMAC), and N-isopropylacrylamide (NIPAm) as functional monomers, divinylbenzene (DVB) as a crosslinker, 2,2′-azobis(2,4-dimethylvaleronnitrile (ADVN) as a radical initiator and a template. Hawkins et al. [14] prepared MIP based on polyacrylamide. They dissolved template, acrylamide, N,N′-methylenebisacryamide, ammonium persulfate in DI water, and added N,N,N′,N′-tetramethylethyleneadiamine as cross-linking agent, finally purged the solution with nitrogen gas for 5 mins to remove oxygen from the solution. The solution was allowed to react for overnight to the MIP. These traditional MIP processes require aggressive free-radical initiators, many reaction steps and long reaction time to prepare MIPs. In addition, these aggressive free-radical initiators and harsh conditions may impair the vulnerable template molecules, including biologically functional molecules such as proteins, DNAs, enzymes, and so on.

Methyl parathion (MP) has been used as a model compound for pesticides and simulants of chemical threat agents. In the past, detection methods of MP include immuno-chemiluminescence [15], colorimetry [16], carbon dot fluorescence [17], optical microbial biosensor [18–20], enzyme biosensor [21–25], electrochemical sensing [21,26–30], and quartz crystal microbalance (QCM) [31,32], etc. Chouhan et al. [15] developed a method based on immuno-chemiluminescence and image analysis using charge coupled device for the detection of MP. They achieved a very low LOD of 0.05 nM. Wang et al. [16] synthesized La^{3+} functionalized Au nanoparticles (NPs) as sensors. They made use of strong coordination effect of La^{3+} to oxygen-containing functional groups such as the methoxy group in MP to induce aggregation of the La^{3+}/Au NPs, which causes color change from red to blue. A low LOD of 0.1 nM was achieved based on colorimetry. Hou et al. [17] reported a fluorescent sensor for MP based on tyrosine methyl ester functionalized fluorescent carbon dots and tyrosinase which could catalytically oxidize tyrosine methyl ester on the surface of carbon dots to quench fluorescence. MP binds to tyrosinase and deactivates it, so the fluorescence of carbon dots is recovered. A very low LOD of 0.05 nM was reported. Kumar et al. [18–20,28] immobilized Flavobacterial sp. or Escherichia coli cells, with or without integrated with polyethyleneimine functionalized silica NPs, on glass fiber filter or polystyrene plate. Flavobacterial sp. and E. coli cells have MP hydrolase which hydrolyses MP to produce p-nitrobenzene which could be quantified with its absorbance at 410 nm or cyclic voltammetry. They reported a LOD of 0.15–0.3 μM. Enzymes acetylcholinesterase (AChE) [21] or MP hydrolase [22–25] were immobilized on different substrates, i.e. AuNPs [24], AuNPs-Polypyrrole [21], CdTe QDs/CNT/AuNPs, Si@AuNPs and multi-walled carbon nanotubes [22], magnetic Fe_3O_4@AuNPs [23], through non-covalent or covalent bonding. AChE catalyzes acetylcholine to produce thiocholine which could be monitored by cyclic voltammetry (CV) or square wave voltammetry (SWV). MP inhibits AChE to reduce thiocholine produced. The lowest LOD achieved with enzymatic voltammetry is 0.3 nM [24]. Electrodes without MP-targeted enzymes for MP detection were also reported, such as AuNPs/Nafion film on glass carbon electrode (GCE) [26], molecular imprinted porous silicate thin film on GCE [27], ZnO/Ag/functional silane/polyester [29], and Ag/graphene nanoribbons on screen printed carbon electrode [30]. The reported LOD are 100 nM, 8.9 nM, 0.07 nM and 3 nM for the above 4 electrodes. Funari et al. [31,32] utilized antibody-antigen-antibody interactions to probe MP antigen by QCM. Antibodies were oriented on the gold surface of a quartz crystal through photonics immobilization technique to enhance the sensitivity so that limit of detection (LOD) 40 nM was achieved for MP.

Enzyme related methods, including immune-chemiluminescence, carbon dot fluorescence, optical microbial biosensors, and enzyme biosensors reviewed above have high sensitivity and selectivity but have limitations on sensor shelf life and cost. Colorimetry is stable but insufficient in selectivity. Electrochemical methods are sensitive and selective but quite tedious in electrode preparation and easily interfered. In this report, we combined the high selectivity of MIP and the high sensitivity of QCM. Conventional MIP technologies utilize hydrophilic polymers such as polyacrylics (polyacrylic acid, poly(mathacrylic acid)), polydopamine, polythiophene, polyimine, or hydrophilic inorganic oxides, such as silica, titania. Hydrophilic MIP sensors have advantages in detecting hydrophilic analyte molecules through hydrogen bonding but have disadvantages in detecting hydrophobic analytes due to lack of strong interactions. Here we demonstrate a hydrophobic PVDF MIP sensor (Scheme 1) for the sensitive and selective detection of hydrophobic analytes through hydrophobic and other interactions.

2. Experimental

2.1. Chemicals and apparatus

Methyl parathion (99.5%) was purchased from Chem Service (West Chester, PA). Parathion ethyl (99.5%), dicrotophos (99.5%), diethyl phosphoramidate (99.5%), Secbumeton (99.5%), 2,4,5-trichlorophenoxy acetic acid, terephthalic acid, dimethylformamide (DMF, 99.5%) and isopropanol (IPA, 99%) were from Sigma (St Louis, MO). Poly(vinylidene fluoride) powder (M.P. 155–160 °C, Mw ~ 180,000 by GPC) was from Alfa Aesar (Ward Hill, MA). QCM sensing platform is a home-made device. 10 MHz AT-cut gold coated quartz crystal discs were purchased from Novaetech s.r.l. (Napoli, Italy), quartz and gold round diameters 15 and 6 mm, respectively. The sensors were characterized by field emission scanning electron microscopy (FESEM) and energy dispersion X-ray spectroscopy (EDS) (JEOL JSM-6701F, Toyko, Japan), Fourier transform infrared spectroscopy (FTIR) (IR Prestige 21 spectrometer, Shimadzu, Kyoto, Japan). UV–vis spectrum was recorded on Hach DR 5000 UV–vis spectroscopy (Hach Co., Loveland, USA), with scanning wavelength of 200–800 nm. Minisart syringe filter with 0.32 μm pore size was purchased from Sartorious stedim biotech GmbH (Geottinggen, Germany).