Sensors and Actuators B 254 (2018) 255–263

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A facile optosensing protocol based on molecularly imprinted polymer coated on CdTe quantum dots for highly sensitive and selective amoxicillin detection

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ARTICLE INFO

Article history:
Received 16 February 2017
Received in revised form 8 July 2017
Accepted 11 July 2017
Available online 15 July 2017

Keyword:
CdTe quantum dots
Molecularly imprinted polymer
Amoxicillin
Photoluminescence

ABSTRACT

A facile method for coating a molecularly imprinted polymer onto CdTe quantum dots (MIP-QDs) was successfully formulated and for the first time used as a highly selective and sensitive photoluminescence probe for the determination of trace amoxicillin. The MIP-QDs were prepared using a sol-gel process with 3-aminopropylethoxysilane as a functional monomer, tetraethoxysilane as a cross-linker and amoxicillin as a template molecule. After removal of the template molecule from the polymer layer, MIP-QDs containing cavities specific to amoxicillin were obtained. The hydrogen bonding between the amino group of 3-aminopropylethoxysilane and functional groups of amoxicillin and the specific size and shape of the cavity provided good selectivity. The photoluminescence intensity of MIP-QDs was more strongly quenched by amoxicillin compared to a non-imprinted polymer (NIP-QDs) with an imprinting factor of 43.6. Under optimum conditions, the photoluminescence intensity of MIP-QDs was decreased in response to increase amoxicillin concentration with good linearity in the range of 0.20–50.0 $\mu g\,L^{-1}$. The limit of detection and the limit of quantitation were 0.14 $\mu g\,L^{-1}$ and 0.46 $\mu g\,L^{-1}$, respectively. The developed method showed good repeatability and reproducibility with the relative standard deviation being less than 6%. This developed method was successfully applied for the determination of amoxicillin in egg, milk and honey samples with a satisfactory recovery of 85–102% being achieved.

1. Introduction

Amoxicillin is a synthetic antibiotic in the β-lactam class of antibiotics and is extensively used to treat infectious diseases in human and animal, being active against both Gram-positive and Gram-negative bacteria [1–3] due to its broad spectrum antibiotic activity and low cost [4]. However, the usage of antibiotics in food-producing animals can lead to the presence of residues in food and the environment [4] which can cause some side-effects such as hypersensitivity in humans [5]. To assure consumer safety, the European Union (EU) has set a maximum residue limit (MRL) of amoxicillin of 50 $\mu g\,kg^{-1}$ in animal tissues and 4.0 $\mu g\,kg^{-1}$ in milk [6]. Therefore, the monitoring of amoxicillin in food products is an important application. Various analytical methods have been developed for the determination of amoxicillin such as chromatography [4,7,8], electrochemical methods [2,3,9], surface plasmon resonance [10] and spectrophotometry [1,11–13]. Among these methods, fluorescence spectroscopy is an interesting alternative method because it has a short analysis time, is relatively simple to use, uses low cost equipment and requires small sample amounts and minimal consumption of organic solvents [12,14]. Several organic dyes have been used as photoluminescence probes to detect various target analytes [15]; however they often have drawbacks such as broad emission bands and mostly asymmetric spectra [16]. To overcome this problems, quantum dots (QDs) have attracted much attention in recent years for use as photoluminescence probes for the determination of ions, molecules, proteins and cells [17–20] due to their desirable optical properties such as size-dependent emission, narrow symmetric emission

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http://dx.doi.org/10.1016/j.snb.2017.07.062
0925-4005/

bands, long photoluminescence lifetime, photochemical stability and good water dispersibility [21,22]. To improve the selectively of this method the surface of QDs need to be modified with target-specific materials [18]. Molecularly imprinted polymers (MIPs) are an attractive strategy to modify the surface of quantum dots. MIPs are affinity polymers and can be synthesized to be specific to a target molecule, they are easy to prepare, inexpensive and display good stability [23]. These materials are highly cross-linked three-dimensional network polymers, formed by polymerization between a functional monomer and a cross-linking monomer whilst including template molecules (target analytes) [24,25]. After the polymerizations were complete, the template molecules were removed and specific cavities were obtained [26]. MIPs combined with QDs have been developed as a photoluminescence probe for a selective determination of some compounds i.e. histamine [27], malachite green [28], chlorpyritos [29] and α-fetoprotein [30].

In this work, molecularly imprinted polymers coated on quantum dots (MIP-QDs) were synthesized and used as a photoluminescence probe for the highly sensitive and selective determination of amoxicillin. The photoluminescence properties and morphology of the synthesized MIP-QDs were investigated and characterized. The effects of various parameters on the analytical performance were also optimized. The developed MIP-QDs were applied for the determination of amoxicillin in egg, milk and honey samples. The developed method was compared with a HPLC method and the recovery from these samples was also investigated.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical grade, amoxicillin, 3-aminopropyl triethoxysilane (APTES, ≥98%), tetraethyl orthosilicate (TEOS, ≥99%), tellurium powder (99.8%), thioglycolic acid (TGA) and sodium borohydride ($NaBH_4$) were purchased form Sigma-Aldrich (St. Louis, MO, USA). $CdCl_2{\cdot}2H_2O$ was purchased from Asia Pacific Specialty Chemicals Co. Ltd. (NSW, Australia). Tris (hydroxymethyl) aminomethane and ethanol (≥98%) were purchased from Merck (Frankfurt, Germany). Ammonia and sodium hydroxide were purchased from RCI Labscan (Bangkok, Thailand). Ultrapure water was from a water purification system (18.2 MΩ cm^{-1}) (Elgastat Maxima, ELGA, UK)

2.2. Instrumental

Fluorescence spectroscopy was performed using a Shimadzu RF-5301PC spectrofluorophotometer (Kyoto, Japan). UV/Vis absorption spectra were recorded using an Avaspec 2048 spectrometer (Avantes, Apeldoorn, Netherlands). The morphologies of MIP-QDs and NIP-QDs were obtained using a scanning electron microscope (JSM-5200, JEOL, Tokyo, Japan) and the FTIR spectra were recorded using KBr pellets in a FTIR spectroscopy (PerkinElmer, Waltham, MA, USA). TEM images were obtained from a TECNAI T20 G^2 transmission electron microscope (FEI, The Netherlands). BET surface areas of MIP-QDs and NIP-QDs were determined using Quantachrome Autosorb 1 system (Quantachrome Instruments, USA).

2.3. Synthesis of TGA- capped CdTe QDs

TGA-capped CdTe quantum dots were synthesized using a method modified from previous work [17,18]. Firstly, 50 mg of tellurium powder and 40 mg of $NaBH_4$ were dissolved in 1.0 mL of deionized water and stirred under a nitrogen atmosphere to prepare a NaHTe solution. Also, 0.05 g of $CdCl_2$ and 25 μL TGA were dissolved in 100 mL of deionized water and adjusted to pH 11.5 with 1.0 M NaOH. Then, this solution mixture was placed into a three-necked flask and deaerated by bubbling with nitrogen gas for 15 min. Under vigorous stirring, 500 μL of NaHTe solution was rapidly injected into the solution mixture under a nitrogen atmosphere. Then the solution was refluxed for 10 min at 90 °C. After being cooled to room temperature, the resulting product was precipitated with ethanol to remove excess reagents and centrifuged at 3500 RCF for 10 min. The obtained TGA-capped CdTe QDs were dried in an oven at 40 °C for 1 h and kept in a desiccator for further use.

2.4. Synthesis of molecularly imprinted polymer coated CdTe quantum dots (MIP-QDs)

The MIP-coated QDs were synthesized via a sol-gel copolymerization process. Briefly, 6.6 mg of amoxicillin (template) was dissolved in 5.0 mL of deionized water and mixed with 30 μL APTES (functional monomer) in a brown bottle and stirred at room temperature (25 °C) for 1 h. Then, 15 mL of TGA-capped CdTe QDs (7.5×10^{-5} M), 135 μL of TEOS (cross-linker) and 150 μL of 25% ammonia solution were added and continuously stirred for 6 h. The resultant products were collected by centrifugation at 3500 RCF for 10 min and washed three times with 10 mL of ethanol to remove template molecules, no amoxicillin (template) could be detected in the washing solvent (ethanol) by UV spectroscopy. Finally, the MIP-QDs were dried in an oven at 40 °C for 1 h. The non-imprinted polymer coated QDs (NIP-QDs) were also prepared through the same procedure but without addition of the template molecule.

2.5. Photoluminescence measurements

Photoluminescence measurements were performed using a spectra band pass of the excitation and emission of 10 nm, an excitation wavelength of 355 nm and recording the emission in the range of 400–700 nm. MIP or NIP-coated QDs (6.0 μg L^{-1}) were dispersed in 10 mM of Tris-HCl buffer solution (pH 8.0). The measurements were obtained by mixing of 150 μL of MIP-QDs or NIP-QDs solution with 50 μL of amoxicillin solution or sample solution. After incubation under gentle rotation for 30 min, the mixture solution was transferred into a quartz cuvette and the photoluminescence intensity was recorded using a fluorescence spectrophotometer. All measurements were performed at room temperature (25 °C) for convenient analysis.

2.6. Sample preparation of food samples

All samples were purchased from the local market in Hat Yai, Songkhla, Thailand. Milk samples were pretreated according to the previous report [31]. Briefly, 30 mL of raw milk was transferred to a 50 mL polypropylene centrifuge tube and centrifuged at 1260 RCF for 15 min to precipitate fat. Then 10 mL of acetonitrile was added into the defatted milk to deproteinize it. Subsequently, the mixture was vortexed and centrifuged at 2240 RCF for 15 min. Then, the supernatant was collected and evaporated to dryness at 40 °C. The extract was redissolved with 2.0 mL of phosphate buffer and analysed by the developed method. For honey samples, the sample preparation was modified from previous work [3]. Briefly, 10 mL of honey was transferred to a 50 mL polypropylene centrifuge tube and diluted with 10 mL of distilled water. The mixture was then vortexed for 1 min followed by centrifuging at 2240 RCF for 20 min and the supernatant was evaporated at 60 °C. Then, 2.0 mL of phosphate buffer was added and vigorously vortexed for 10 s before analysis. The preparation of egg sample was modified from previous work [4], whole egg white was homogenized and 5.0 g of homogenized egg was transferred into a 50 mL polypropylene centrifuge tube and 10 mL of acetonitrile was added. The mixture was extracted by ultrasonification for 15 min and then centrifugation at 2240