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A molecularly imprinted polymer based a lab-on-paper chemiluminescence device for the detection of dichlorvos

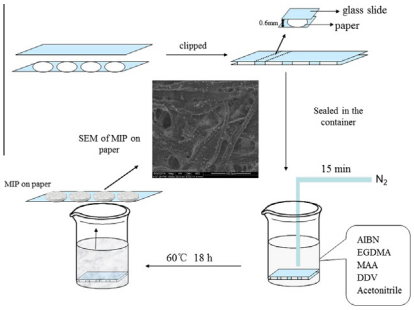
Wei Liu *, Yumei Guo, Jing Luo, Juan Kou, Hongyan Zheng, Baoxin Li, Zhujun Zhang

Key Laboratory of Analytical Chemistry for Life Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China

HIGHLIGHTS

- The MIP layer against dichlorvos (DDV) was synthesized and adsorbed on the paper.
- The paper-based device was fabricated by a low-cost cutting method.
- DDV can greatly enhance the CL signal of luminol-H_2O_2 system.
- The detection limit for DDV was 0.8 ng mL^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a new molecularly imprinted polymer (MIP) based lab-on-paper device with chemiluminescence (CL) detection of dichlorvos (DDV) was designed. With the circle-shaped device, the MIP layer with certain depth was synthesized and adsorbed on the paper surface and DDV can be selectively imprinted on it. The adsorption and washing procedures can be achieved well on the paper-based chip. The paper-based device was fabricated by a simple cutting method and many chips can be made at the same time. On the basis of DDV enhancing CL of luminol-H_2O_2 greatly, the proposed MIP based lab-on-paper CL device showed better selectivity to DDV and it has been applied to the determination of DDV in vegetables in the range of 3.0 ng/mL–1.0 μg/mL with the detection limit of 0.8 ng/mL. This study has made a successful attempt in the development of highly selective and sensitive monitoring of DDV in real samples and will provide a new approach for sensitive and specific assay in environmental monitoring.

Introduction

Microfluidic paper-based analytical devices (μPADs), which combine the simplicity of paper strip tests and the complexity of the conventional lab-on-paper devices, have gained more and more attention during the recent years [1,2]. Paper has the advantage of being relatively cheap, biodegradable and abundant, so high speed coating and printing techniques can be available on paper [3]. For the detection method for μPADs, colorimetric method is the primary detection method for the qualitative and quantitative analysis of multiple analytes [4–6]. However, it cannot meet the demands of lower detection limit and new detection methods with higher sensitivity such as electrochemical [7–11] and chemiluminescent methods [12–16] used recently on μPADs. Chemiluminescence (CL) has gained much attention for a powerful analytical tool on μPADs [2] because it can provide higher sensitivity and less instrumentation. To improve the selectivity of the detection method, different separation method or specific identification method was chosen to be used on μPADs. Our group has reported the work by using the paper chromatography method for DDV detection on μPADs [13]. After sample developing, DDV can be

* Corresponding author. Tel.: +86 29 81530726; fax: +86 29 81530727.
E-mail addresses: weiliu@126.com, liuwei2@hotmail.com (W. Liu).

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detected on μPADs without complicated sample preparation in vegetables. Two specific identification methods of oxidase enzyme reactions and immunoassay with CL detection were mostly used on the paper-based chip [12,14–16] which can improve the selectivity for CL. To an extent, there is a trend to establish some new specific identification method with CL detection on μPADs.

Recently, polymer-based sensor [17–19] has been a promising field which can be used in medical diagnostics, environmental monitoring and pharmaceutical bioassays. Among these polymers, molecular imprinting technique has become a well-known technology for the preparation of biomimetic recognition matrices which have very selective binding sites in highly cross-linked macroporous polymers. [20] They have specific recognition function and have been utilized in μPADs [21–24]. Yu et al. [22–24] has reported that MIPs can be electropolymerized on Au nanoparticle (AuNP)-modified paper working electrode on the paper-based chip and these were the first reports to introduce MIP technology into μPAD with electrochemical detection method. They also [25] used paper-based MIP-grafted multi-disk micro-diskplate for sensitive and specific CL detection of 2,4-dichlorophenoxyacetic acid. In their work, paper surface was activated first and MIP was synthesized on the paper surface by using the in situ polymerization method. But the main problem is that the depth of the MIP layer cannot be controlled very well by using this method. In addition, the authors did not introduce the chemical mechanism of MIP reacting with the cellulose. While, in our work, the modification or activation procedure was not needed with paper and MIP layer was adsorbed on the paper surface by physical adsorption. The depth of the MIP layer can be easily controlled on the paper surface which can provide the precision and specificity toward the DDV detection.

Pesticides have been used worldwide in agriculture for many years to protect plants and prevent crop damage [26]. DDV belongs to organophosphate (Ops) pesticide which can occasionally involve in food extortion threats and formerly used as neurotoxins in chemical warfare. Gas and liquid chromatography coupled to mass spectrometry (GC–MS (/MS) or LC–MS (/MS)) are generally used [27–29] for the identification and quantification of pesticides. Besides, CL has been revealed as an excellent tool for Ops detection [30] and a highly sensitive CL assay for the detection of DDV pesticide was developed by Zhang et al. [31] using the luminol-H_2O_2 CL system. DDV could generate CL emission directly when it was reacted with luminol and H_2O_2. Hence, the luminol CL system can be used for DDV detection with higher sensitivity. In our group's former work [13], DDV was developed first on μPADs and detected by the upper CL system. By using the same CL sensing mechanism in this work, DDV was selectively recognized first on μPADs and detected with the higher sensitivity.

In this work, DDV was detected for the first time on MIP-based lab-on-paper device with a sensitive CL detection method. The MIP layer was adsorbed on the paper surface with well-controlled depth. The paper-based chip can be specific and selective for the determination of DDV in the samples with the detection limit of 0.8 ng/mL. It was found that the proposed paper-based chip provides a number of advantages such as high sensitivity, high selectivity and simple operation for the determination of DDV. This new MIP based lab-on-paper CL device is especially useful for on-site environmental testing of pesticides, drugs or environmental pollutants in remote regions.

Experimental

Materials and reagents

All chemicals were of analytical grade and used without further purification. Methacrylic acid (MAA) was purchased from Tianjin Kermel Chemical Reagent Development Center (China). Azobisisobutyronitrile (AIBN) was purchased from Shanghai chemical Co, Ltd. (China). Ethylene glycol dimethacrylate (EGDMA) was purchased from Sigma–Aldrich (USA). The Ops pesticide standard solutions were prepared from the Agro-Environment Protection Institute (Tianjin, China). Hydrogen peroxide, ethanol, acetic acid, acetone, acetonitrile were obtained from Xi'an Chemical Co., Ltd. (China). Methanol was purchased from Fisher Scientific (America) which was chromatographic grade. Whatman chromatography paper 3 MM CHR (20.0 cm × 20.0 cm) was obtained from GE Healthcare Worldwide (Pudong Shanghai, China) and used with further adjustment of size. A 0.25 mol/L luminol solution was prepared by dissolving 4.43 g of luminol (Kangpei Technology Co., China, 98%) in 100 mL of 0.5 mol/L NaOH solution. A stock solution of 1.0 mol/L H_2O_2 was freshly prepared everyday by diluting 5.5 mL of 30% (v/v) hydrogen peroxide to 50 mL with water.

Instrumentation

The CL intensity was detected by the IFFL-D type FI-CL analyzer (Xi'an Remax, China). The scanning electron microscope (SEM) microphotographs of MIPs were performed on Quanta 200 (FEI, USA). The paper was cut by cutting plotter which was made by Graphtec CE-5000 (Japan). UV absorption spectra were measured on a UV-1800 spectrophotometer (Shimadzu, Japan).

Preparation of MIP on paper-based chip

The MIPs for DDV were prepared based on previously reported methods [32,34]. 1.0 mmol/L DDV which was dissolved in acetone was mixed with 4.0 mmol/L MAA in a 100 mL flask. The mixture was surged ultrasonically for 5 min. Afterward 20.0 mmol/L EGDMA, 14 mg AIBN and 60 mL acetonitrile were added. The mixture was surged ultrasonically for 5 min. Then the solution was purged with nitrogen for 15 min and the flask was sealed directly for polymerization at 60 °C in a water bath for 18 h. To eliminate even traces of the template and the unreacted monomers from the MIPs, these were washed with a 1:9 (v/v) mixture of acetic acid and methanol until no traces of DDV were detected. The purity of washing solvents was checked with UV. Then, the MIPs were dried to a constant weight at 60 °C under vacuum. The non-imprinted polymers (NIPs) were also synthesized following exactly the same procedure, but excluding the template DDV from the formulation.

The paper used in this work was Whatman chromatography paper 3 MM CHR (20.0 cm × 20.0 cm). Using the Graphtec Cutting machine (Graphtec CE-5000-40-CRP, Japan), the paper was cut into a circle with the diameter of 8.0 mm. The circle-type paper was clipped between two glass slides (Fig. 1) and was stuck to the surface of the bottom glass slide. To make the gap in the two glass slides, water impermeable double-sided tape with the depth of 600 μm was stuck to the four corners of the bottom glass slide. Then the upper glass slide was aligned and covered on the bottom glass slide. There was a gap of 600 μm between the two glass slides. The depth of MIP layer on the paper was controlled directly by this gap between the two slides. Two clips were used here for fixing the two glass slides together. The glass slides with the circle-type paper inside were put inside a 50 mL flask. Then DDV, MAA, EGDMA, AIBN and acetonitrile were added into the flask with the same amount as above. After the polymerization for 18 h, the glass slides were taken out and put into the soxhlet extraction. The polymer was washed with 300 mL of methanol containing 10% acetic acid to eliminate the template from MIP, which was verified by analysis of the methanol eluent using high performance liquid chromatography (HPLC) at 215 nm. Finally, the two clips were taken away from the glass slides and the MIP-based paper