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Simple and sensitive detection of pesticides using the liquid crystal droplet patterns platform

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ABSTRACT

The alignment of liquid crystal (LC) is known to be sensitive to the properties of a bounding interface. Here, we report a LC droplet pattern platform based on enzymatic event of acetylcholinesterase (AChE) for sensitive detection of pesticides. In this method, the dark cross appearances of LC droplet patterns are obtained due to the formation of myristoylcholine (Myr) monolayer at the aqueous/LC interface after transferring Myr solution, which is corresponding to the perpendicular alignment of LC molecules at the interface. On the one hand, AChE mediates the hydrolysis of Myr to disrupt the surfactant monolayer, and the process leads to the bright fan-shaped images of LC droplet patterns when in contact with the pre-incubated mixture of AChE and Myr, which is indicating a planar orientation of LCs at the interface. On the other hand, the hydrolysis of Myr is inhibited in the presence of AChE-inhibiting pesticides such as baycarb and dimethoate, as a result, the LC droplet patterns present the dark cross appearances. On the basis of the principle, the LC droplet patterns could be utilized as an effective method to detect the pesticides. The results demonstrated that the LC droplet patterns were sensitive to baycarb with a detection limit of 1 ng/mL and dimethoate with a detection limit of 0.1 ng/mL. The constructed LC-based sensing platform is quite simple and convenient, and shows high promise for label-free detection of pesticides with very high sensitivity.

1. Introduction

Carbamates and organophosphates are class of compounds frequently used as pesticides, which are useful to control agricultural pests. However, pesticides are also toxic to animals and aquatic vegetation as the acetylcholinesterase (AChE) inhibitors [1–5], because of cholinergic transmission's universally occurring. Due to the extensive use of AChE-inhibiting pesticides resulted in many ecotoxicological problems, European Union developed strict regulates in the emission and discharge of pesticides [6,7]. Besides, the abuse and public safety concern regarding pesticides also made it increasingly imperative to construct a fast, convenient and sensitive platform for detection of pesticides. Array sensing methods have been developed to monitor pesticides by conventional analytical methods, such as mass spectrometry [8], chromatography [9], fluorometry [10], colorimetry [11], and electrochemistry [12]. Although these methods have contributed to detecting pesticides, they have several limitations as well, i.e., the systems reported so far critically depend on excessive labor resources, expensive and complex instrumentations, specialized molecular probes and a lengthy operating time. Therefore, simple methods with high sensitivity and stability are highly desirable.

Liquid crystals (LCs) have been generally used as promising sensing platform for monitoring the chemical and biological events [13,14]. We have previously demonstrated that a LC sensing platform decorated with myristoylcholine chloride (Myr) is able to realize the detection of AChE and its inhibitor [15]. And it has been developed methods for detecting organophosphates based on LC sensors. For example, Li's group constructed a novel LC-based sensor that could identify around 0.51 mg/m^3 dimethyl methylphosphonate vapors [16]. Chen et al. developed the LC sensing platform through the localized pH changes induced by organophosphates hydrolytic products with a detection limit for paraoxon as 1 μM [17]. Both of the systems provide novel approaches for sensitive detection of organophosphates. Recently, LC droplet patterns have been considered as an effective platform among the LC-based sensors, because the large surface-area-to-volume ratio to increase the detection sensitivity by facilitating

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the reorientation of LC molecules at the interface [18,19]. The LC patterns showed dark cross appearances when in contact with surfactant solutions, whereas bright fan-shapes were acquired after introducing deionized water. For example, Hu et al. examined the spontaneous formation and application of LC droplet patterns as sensors [20,21].

Inspired by the above work, we constructed a LC droplet platform decorated with cationic surfactant to detect pesticides in a convenient and sensitive way in this study. The design and process of pesticides LC sensors based on enzymatic hydrolysis of Myr is depicted in Fig. 1. The dark cross appeared after introducing Myr solutions, coupling to the homeotropic orientation of LC molecules at the aqueous/LC interface. This suggests that the Myr monolayer formed at the aqueous/LC interface because of the hydrophobic interaction between Myr and LCs (Fig. 1a). The LC patterns turned into the bright fan-shape images upon addition of pre-incubated mixture of Myr and AChE, which indicates that the Myr monolayer could not form due to enzymatic reaction between AChE and Myr (Fig. 1b). What is interesting is that the LC droplet patterns still displayed dark cross appearances after introducing Myr pre-incubated with the mixture of pesticides and AChE. Moreover, the sensitivity of this system for pesticides was investigated based on the optical response of the LC droplet patterns. Comparing to the existing LC sensing techniques for detection of pesticides, this system can detect aqueous solutions of interests as low as 0.1 μL, which enables simple and convenient detection of pesticides with low cost and high sensitivity.

2. Materials and methods

2.1. Materials

Nematic liquid crystal 4-cyano-4′-pentybiphenyl (5CB), octadecyltrichlorosilane (OTS), heptane, dimethoate and baycarb were purchased from J&K Scientific Co., Ltd. Acetylcholinesterase (AChE), phosphate buffered saline (PBS) (10 mM phosphate, 138 mM NaCl, 2.7 mM KCl; pH 7.4) were obtained from Sigma-Aldrich. Myristoylcholine chloride (Myr) was purchased from Shanghai Shfeng Biological Technology Co., Ltd. of China. Sulfuric acid, hydrogen peroxide (30% w/v), and bovine serum albumin (BSA) were obtained from Shandong Aibo Technology Trade Co., Ltd., China. Cellulase was purchased from Beijing Jingke Hongda Biotechnology Co., Ltd., and pectinase was obtained from Beijing Solarbio Science & Technology Co., Ltd. of China.

2.2. Treatment of OTS-coated glass slides

Glass microscope slides were prepared according to the previous literatures [22,23]. In brief, the glass slides were cleaned with "piranha solution" (70% H_2SO_4/30% H_2O_2; warning: "piranha solution" reacts violently with organic substance and should be handled with extreme caution; do not store the solution in closed containers.) for 30 min at 80 °C. They were then rinsed with water, ethanol, and methanol, and dried sequentially under a steam of gaseous N_2, followed by heated to 120 °C overnight. The "piranha-cleaned" glass slides were immersed into the OTS/heptane solution for 30 min at room temperature. They were then rinsed with methylene chloride and dried under a stream of N_2.

2.3. Assays for AChE activity and inhibition

In the assay of enzyme inhibition, a mixture of pesticides and AChE was pre-incubated at 37 °C for 15 min. Then the aqueous solutions containing 8.27 U/mL AChE and different concentration of pesticides were continued to be incubated at 37 °C for 15 min after introducing 0.1 mM Myr. All aqueous solutions related to enzymatic reactions were prepared in PBS (10 mM phosphate, 138 mM NaCl, 2.7 mM KCl; pH 7.4). For the determination of pesticides in the environment of lake, filtered water sample from Daming Lake was used without any further purification.

2.4. Preparation of LC droplet patterns

LC droplet patterns supported on OTS-treated glass slides were formed by dropping 1 μL 5CB (1% in anhydrous heptane, v/v) onto the glass surface. After evaporation of the organic solvent, aqueous solutions of interest were introduced onto the LC droplets at room temperature. Noteworthy is that the detection limit reaches 0.1 μL.

2.5. Optical examination of LC textures

A polarized light microscope (XPF-800C, Tianxing, Shanghai, China) was used to observe the optical texture of 5CB with the polarized light transmitting through LC droplet patterns. The images were obtained by a digital camera (TK-9301EC, JVC, Japan) at room temperature.

3. Results and discussion

3.1. Optical response of LC droplet patterns to myristoylcholine chloride

It has been reported that spontaneous formation of LC droplet patterns with large surface areas occurs on glass microscope slides [20]. Stable LC droplet patterns were formed by dropping 5CB (1% v/v) dissolved in anhydrous heptane onto the OTS-coated glass slide after the solvent evaporated. In order to investigate the fesibility of LC droplet patterns for detecting pesticides, we first studied the optical behaviors of 5CB at the aqueous/LC interface in contact with Myr solutions. We compared the optical response of LC droplet patterns in contact with PBS and Myr solutions. The bright fan-shaped images were obtained after incubating the LC droplet patterns with PBS solution; this can be attributed to the planar orientation of LCs at the aqueous/LC droplet interface (Fig. 2a). In contrast, in the case of adding 1 mM Myr, LC droplet patterns presented the dark cross appearances, which suggested the homeotropic alignment of 5CB at the aqueous/LC interface (Fig. 2b). In this case, the homeotropic anchoring was attributed to the self-assembled Myr monolayer formed at the aqueous/LC interface, which is consistent with our previous report [15]. We also monitored the transition of optical appearances by lowing the concentration of Myr. The LC droplet patterns showed dark cross appearances in contact with 0.1 mM Myr (Fig. 2c) and bright fan-shape images as 0.01 mM Myr transferring onto the interface (Fig. 2d). We concluded that the critical concentration of Myr to turning the LCs into dark crossed optical texture was around 0.1 mM. On the basis of these results, we predict that the optical images of LC droplets would be changed upon introducing AChE, because the monolayer will be hydrolyzed. Subsequently, we chose 0.1 mM Myr for the further research on the activity of AChE and detection of pesticides.

3.2. Feasibility and specificity of AChE detection platform on LC droplet patterns

To validate the above speculation, we investigated the orientational transition of LC patterns in contact with the pre-incubated mixture of AChE and Myr in PBS. The LC droplet patterns displayed bright fan-shape images after transferring mixture of AChE (82.7 U/mL) and Myr (0.1 mM), which represented a planar orientation of the LCs at the aqueous/LC interface. Under the circumstances, the planar orientation arose from the enzymatic