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A nonionic surfactant-decorated liquid crystal sensor for sensitive and selective detection of proteins

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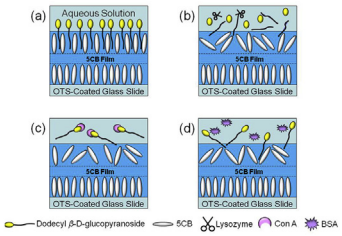
HIGHLIGHTS

- A label-free LC-based sensor with high selectivity and sensitivity for protein detections.
- Three proteins including lysozyme, Con A and BSA are detected based on three different mechanisms.
- A nonionic surfactant-decorated liquid crystal interface as the sensing platform.
- The surfactant monolayer is stable regardless of pH and ionic strength in a wide range.

GRAPHICAL ABSTRACT



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ABSTRACT

Proteins are responsible for most biochemical events in human body. It is essential to develop sensitive and selective methods for the detection of proteins. In this study, liquid crystal (LC)-based sensor for highly selective and sensitive detection of lysozyme, concanavalin A (Con A), and bovine serum albumin (BSA) was constructed by utilizing the LC interface decorated with a nonionic surfactant, dodecyl β-D-glucopyranoside. A change of the LC optical images from bright to dark appearance was observed after transferring dodecyl β-D-glucopyranoside onto the aqueous/LC interface due to the formation of stable self-assembled surfactant monolayer, regardless of pH and ion concentrations studied in a wide range. The optical images turned back from dark to bright appearance after addition of lysozyme, Con A and BSA, respectively. Noteworthy is that these proteins can be further distinguished by adding enzyme inhibitors and controlling incubation temperature of the protein solutions based on three different interaction mechanisms between proteins and dodecyl β-D-glucopyranoside, viz. enzymatic hydrolysis, specific saccharide binding, and physical absorption. The LC-based sensor decorated with dodecyl β-D-glucopyranoside shows high sensitivity for protein detection. The limit of detection (LOD) for lysozyme, Con A and BSA reaches around 0.1 μg/mL, 0.01 μg/mL and 0.001 μg/mL, respectively. These results might provide new insights into increasing selectivity and sensitivity of LC-based sensors for the detection of proteins.

1. Introduction

Proteins are of great importance in medical and environmental

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fields. Development of simple and robust methods for highly selective and sensitive detection of proteins is essential in many biological applications and clinical diagnosis [1,2]. Enzyme-linked immunosorbant assays (ELISAs) are used as the classical methods to monitor proteins [3,4]. Additionally, fluorescent approaches [5], electrochemical methods [6] and spectrophotometry [7] have been applied broadly in detection of proteins. However, many of these methods encounter drawbacks such as inaccessible labeled molecules, intensive labor, complex instrumentation, and long prepared time. In the past decade, biosensors based on liquid crystals (LCs) have drawn the researchers' great interest in detecting biological molecules [8–11] due to their unique properties such as high sensitivity to the changes on the interface, amplification of the signal, low cost, simplicity and rapid response [12–14]. In particular, LC-based sensors show potential in the application of protein assays. For example, Fang's group modified the interface of 5CB droplets by adsorption of polyelectrolytes and then demonstrated the detection of bovine serum albumin (BSA) through electrostatic interactions between the polyelectrolytes and BSA [15]. Pal et al. reported that the interface of LCs decorated with lipopolysaccharide monolayer could be applied to detect hemoglobin, BSA and lysozyme [16]. Park's group constructed the LC microdroplets coated with polyacrylic acid block liquid crystalline polymer for the detection of lysozyme and BSA [17]. In addition, they also designed LC interfaces decorated with polyelectrolytes to detect proteins such as BSA, lysozyme, and hemoglobin [14,18,19]. However, selectivity and sensitivity of LC-based sensors still have to be largely improved for protein assays.

In the previous reports, surfactants have been widely applied in constructing sensing platforms at the aqueous/LC interfaces, LC-based sensors constructed by nonionic surfactants were seldom demonstrated. However, nonionic surfactants have the potential to improve performance of the LC-based sensors as they are lack of positive or negative headgroups, which enables them to form highly stable monolayers at the aqueous/LC interface in broad pH and salt tolerance. In this study, we developed a label-free LC-based sensing platform decorated with nonionic surfactant, dodecyl β-D-glucopyranoside, to detect three different proteins viz. lysozyme, concanavalin A (Con A) and BSA with high sensitivity and selectivity. The formation of a stable monolayer of dodecyl β-D-glucopyranoside formed at the aqueous/LC interface drives the transition of LC molecules from planar (Fig. 1a) to homeotropic alignment (Fig. 1b) at the aqueous/LC interface, which couples to the optical appearance of LCs from bright (Fig. 1c) to dark (Fig. 1d) appearance. Although the proteins could be screened based on changes of the optical images from dark to bright appearance after adding each of the analytes separately, these proteins can still be selectively recognized based on their different interaction mechanisms with dodecyl β-D-glucopyranoside. Lysozyme could be differentiated by incubating the enzyme with 1-methylimidazole due to inactivation of lysozyme, and BSA could be distinguished by heating-induced change of the protein, but both of the factors have no effect on Con A. In comparison with the existing methods, this novel approach provides a very simple, low-cost, and lable-free sensing platform and exhibits a promising prospect in the construction of highly selective and sensitive LC-based platform for researching protein assays.

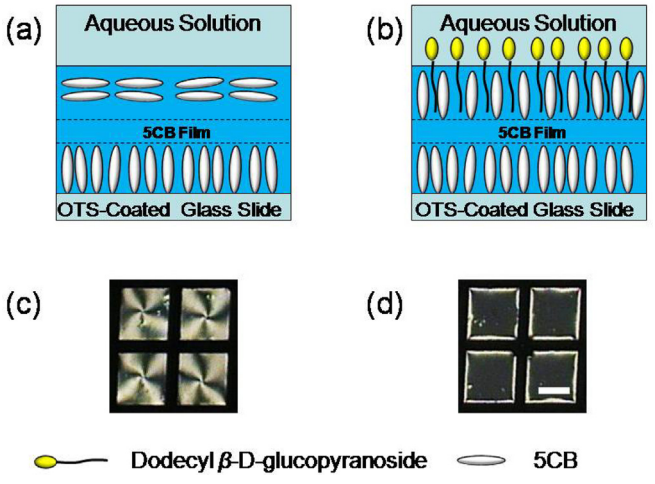

Fig. 1. Schematic illustration of orientation of LCs in contact with the dodecyl β-D-glucopyranoside at the aqueous/LC interface: (a) planar orientation, (b) perpendicular orientation. The corresponding optical appearance associated with the orientation of LCs: (c) bright appearance and (d) dark appearance. Scale bar: 400 μm.

2. Experimental

2.1. Materials

Nematic liquid crystal 4-cyano-4′-pentylbiphenyl (5CB), octadecyltrichlorosilane (OTS), heptane, 1-methylimidazole and D-(+)-glucose were obtained from J&K Scientific Co., Ltd., China. Phosphate buffered saline (PBS) (10 mM phosphate, 138 mM NaCl, 2.7 mM KCl; pH 7.4) was purchased from Sigma-Aldrich. Bovine serum albumin (BSA) was obtained from Shandong Aibo Technology Trade Co., Ltd., China. Fluorescein isothiocyanate (FITC) was obtained from Aladdin Chemistry Co., Ltd., China. Dodecyl β-D-glucopyranoside, lysozyme, concanavalin A (Con A), and BSA labeled with FITC were supplied by Shanghai Shfeng Biological Technology Co., Ltd., China. Gold specimen grids (75 mesh, pitch = 340 μm, bar = 55 μm, hole = 285 μm) were purchased from GILDER.

2.2. Preparation of glass microscope slides

The glass substrates used in this study were prepared according to the procedure reported earlier [20,21]. Briefly, glass microscope slides were first cleaned by "piranha solution" (70% H_2SO_4/30% H_2O_2) for 30 min at 80 °C. [Caution: "piranha solution" reacts violently with organic substance and should be handled with extreme caution; do not store the solution in closed containers.] The slides were then rinsed thoroughly with water, ethanol, and methanol, respectively, and then dried under a steam of gaseous N_2, followed by heating to 110 °C overnight prior to OTS coated. The "piranha-cleaned" glass slides were immersed in the OTS/heptane solution for 30 min. Then, they were rinsed with methylene chloride and dried under a stream of N_2.

2.3. Preparation of optical cells

Gold specimen grids were cleaned sequentially in methylene chloride, ethanol, and methanol, dried under a stream of N_2, and then heated to 110 °C overnight. Gold specimen grids were first placed onto the OTS-treated glass slides. Then, ~1 μL of 5CB was dispensed onto each grid, and the excess LC was removed by contacting a 20 μL capillary tube with 5CB on the grid. Subsequently, 200 μL aqueous solutions of interest were introduced into optical cell at room temperature [11]. All the results were repeated at least three times.

2.4. Preparation of aqueous solutions

All aqueous solutions of proteins and inhibitors were prepared in PBS (pH 7.4). The aqueous solutions with different pH and salt