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Optical biosensor based on liquid crystal droplets for detection of cholic acid

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ABSTRACT

A highly sensitive cholic acid biosensor based on 4-cyano-4′-penthlbiphenyl (5CB) Liquid crystal droplets in phosphate buffer saline solution was reported. A radial-to-bipolar transition of 5CB droplet would be triggered during competitive reaction of CA at the sodium dodecyl sulfate surfactant-laden 5CB droplet surface. Our liquid crystal droplet sensor is a low-cost, simple and fast method for CA detection. The detection limit (5 μM) of our method is 2.4 times lower than previously report by using liquid crystal film to detection of CA.

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1. Introduction

Bile acids (mainly contain cholic, deoxycholic, and lithocholic acid) are important steroidal compounds, which are produced in the liver from cholesterol and play a significant physiological role in digestion and absorption of dietary lipids and fat-soluble vitamins through emulsification [1,2]. In addition, cholic acid (CA) is one of primary bile acids as it weighs more than 31% in all of bile acid and the concentration of CA is connected with liver cancer (hepatocellular carcinoma), gallstone and other diseases [3,4]. The concentration of CA is normally in range of 1–5 mM in liver and less than 10 μM in human's serum [5,6]. For these reasons, developing a strategy to detect the concentration level of CA is particularly critical.

In recent years, many methods have been developed for the detection of CA. For example, thin-layer chromatography [7], gas chromatography (GC) [8], supercritical fluid chromatography (SFC) [9], optical spectrum analyzer [10], molecularly imprinted [11], high-performance liquid chromatography (HPLC) and mass spectrometry (MS) [12–14]. However, these methods require expensive instruments and complex operational processes. Low-cost, simple and fast analytical method for cholic acid is highly desirable.

With the development of optical device, more and more optical methods have attracted attentions because of their potential utility with specific, direct detection process, low cost and less time consuming of analysis, compared to conventional assay techniques. Among them, liquid crystal (LC) is a promising candidate of optical biological sensor due to their unique properties of large birefringence and high sensitivity of the orientations of liquid crystal molecules to tiny variation on the surface [15,16]. Molecule events occurred at an LC/aqueous interface can be amplified and transduced through orientation changes of LC molecules into optical signals, which are visible by the naked eye under polarizing optical microscope [17,18].

LC droplets have been widely used in environmental and biomedical science as a sensor with high sensitivity [19,20]. Several research groups have utilized LC droplets for the detection of viruses, bacteria, avidin, cancer cells and protein [21–24]. Merola et al. maneuvered fragmental nematic LC on the substrate surface and achieved different configurations LC droplets in electric field, which can be used as spatial modulation [25]. Hu et al. demonstrated a sensing device, which used to examined water vapors, amphiphiles, and vapors of volatile organic compound (VOCs), where the LC was dissolved in organic solvents on glass microscope slides and distinctive optical textures that represent different orientations of LCs was observed under a polarizing optical microscope [26]. He et al. reported a sensor based on LC layer for detection CA [27]. However, the multilayer of LC leads to a strong anchoring force, which is not easy to be disturbed by CA thus the sensitivity can be furthur improved.

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Herein we proposed a low-cost, simple and fast method for CA detection based on LC droplets. Sodium dodecyl sulfate (SDS) was coated on the surface of 4-cyano-4′-penthlbiphenyl (5CB) liquid crystal droplets, which resulted to a radial configuration of LC droplets in phosphate buffer saline (PBS) solution. A radial-to-bipolar transition of 5CB droplet will be triggered during competitive reaction of CA at the SDS surfactant-laden 5CB droplet surface when certain amount, beyond detection limit, of CA was added. The detection limit (5 μM) of our method is 2.4 times lower than previously report by using liquid crystal film to detection of CA.

2. Materials and methods

2.1. Chemicals and materials

Sodium chloride (NaCl), sodium dodecyl sulfate (SDS, >98%), sodium hydroxide (NaOH), phosphate buffer saline (PBS) (10 mM phosphate, 138 mM NaCl, 2.7 mM KCl; pH 7.4), and cholic acid (CA) were all purchased from Sigma-Aldrich. 4-n-pentyl-4′-cyanobiphenyl (5CB) was bought from HCCH (Jiangsu Hecheng, China). Microscope slides (25.4 mm × 76.2 mm, 1 mm thick) were purchased from Sail Brand (Shanghai, China). Glass cover slides (Sail Brand) were obtained from Taizhou Dongsheng Glass Co. Ltd., China. All aqueous solutions were prepared using double-deionized water obtained from a Millipore Ultra-Pure Reagent Water System (Millipore, Continental Water Systems, ElPaso, TX, USA). All experiments were carried out at 25 °C.

2.2. Preparation and observation of liquid crystal droplets

Microscope glass slide was cleaned using a hot piranha solution (H_2SO_4 (98%): H_2O_2 (35%)=3:1) for 30 min (caution: piranha solution is extremely corrosive and must be handled carefully). Then it was washed with deionized water and dried under nitrogen. Acrylic ab adhesive was used as rampart paint on the functionalized glass slide. Optical images of LC droplets were observed using polarizing optical microscope (Ti 200, Nikon) in transmission mode.

3. Results and discussions

3.1. Fabrication of LC cell

A LC cell with thickness of 200 μm and size of 10 × 10 mm was assembled by a glass side and a coverslip, sealed by acrylic AB adhesive as in Fig. 1(a). Sodium dodecyl sulfate (SDS) is a kind of surfactant, coated by oleophilic long alkyl chain and hydrophilic chemical group. When LC droplets contacted with SDS in the PBS solution, the SDS will adhere to the surface of LC droplets due to their oleophilic long alkylchain, leading to the formation of SDS-laden 5CB droplet/aqueous surface. This reaction is illustrated in Fig. 1(b). Due to good hydrophobicity of 5CB, a nematic liquid crystal (5CB here) droplet naturally acquires a spherical shape with an internal radial director configuration when dispersed in SDS. The polarizing optical microscope image showed typical cross dark lines in droplets, as shown in Fig. 1(c).

When CA is added into the solution containing 5CB droplets with SDS-Laden surface, a radial to bipolar configuration would be triggered. The reason is that the CA prefers to adsorb at the surface of LC molecule through the interface competitive adsorption with the SDS-laden 5CB droplet/aqueous, which leaded to a change in LC droplets and became bipolar configuration. The schematic and polarizing optical microscope image of bipolar configuration is shown in Fig. 1(d), where a dark line is observed in bipolar configuration.

3.2. Preparation of LC droplets

According to Oscar's report, droplets should fragmentate from a large size to small in a criticality condition [28]. In forming process of LC droplets, the size of LC droplets depends on the stirring time in mixing. Fig. 2(a)–(e) shows polarization optical microscopy images of 5CB droplets with different stirring time of 6 s, 60 s, 120 s, 180 s, and 240 s, where the stirring speed is 600 rpm and the volume ratio of LC and SDS is 1:15. Fig. 2(f) shows the different diameters obtained under different stirring time. The size of LC droplets decreases with the increase of stirring times increased. After mixing, the mixture was injected into the LC cell with 10 mM of PBS.

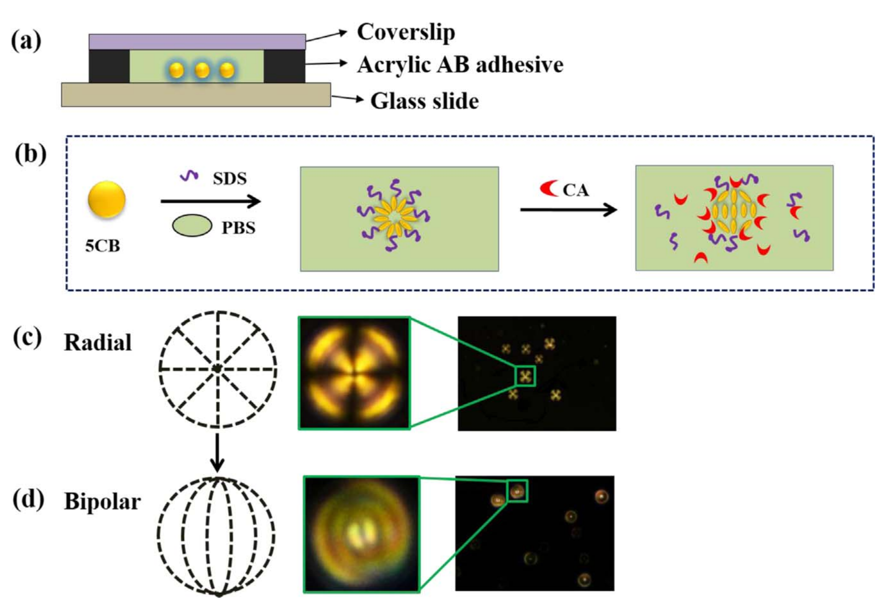

Fig. 1. (a) Liquid crystal cell structure; (b) schematic illustration of the competition absorption of CA at the SDS-laden 5CB droplet/aqueous surface; (c) radial configuration and corresponding polarization optical microscopy image of 5CB droplets without CA in PBS solution; (d) bipolar configuration and polarization optical microscopy image of 5CB droplets with CA in PBS solution.

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