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Real-time liquid crystal-based glutaraldehyde sensor

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ABSTRACT

We develop a liquid crystal (LC)-based optical sensor for detecting glutaraldehyde vapor by using real-time orientational responses of 4-cyano-4′-pentylbiphenyl (5CB) to glutaraldehyde. The sensor comprises a thin layer of 5CB (~20 μm) supported on an amine-decorated surface. When a glutaraldehyde molecule diffuses through the layer of 5CB, it reacts with a surface amine group and forms an imine bond. Subsequently, the resulting free aldehyde group from the glutaraldehyde molecule triggers an orientational transition of 5CB, which manifests as an optical signal visible to the naked eye. Because the performance of the LC-based sensor critically depends on the diffusion of glutaraldehyde in 5CB, we also measured the solubility and diffusivity of glutaraldehyde in 5CB. Based on the diffusivity, an optimal LC sensor with a 20-μm-thick film of 5CB can respond to 207 ppmv glutaraldehyde within 20 s and shows a full response in 4 min. It also shows good specificity. Only a very weak response is observed when this sensor is exposed to acetic acid, and no response is recorded for methanol, ethanol or formaldehyde.

1. Introduction

Glutaraldehyde is a versatile compound which has been used in large quantities for many applications, such as sterilization, crosslinking biomolecules and chemical synthesis [1–3]. Routine exposure to glutaraldehyde, however, is known to cause severe health effects. To prevent the accumulation of glutaraldehyde in working environments, it is necessary to design a glutaraldehyde sensor for real-time monitoring vaporous glutaraldehyde in the atmosphere. Currently, there are several methods readily available for detecting glutaraldehyde, such as by using a 2,4-dinitrophenylhydrazine impregnated cartridge followed by high-performance liquid chromatography analysis [4,5], or by using an electrochemical fuel cell sensor [6]. Nevertheless, these methods require laboratory-based instrumentation, which limits their applications as a portable glutaraldehyde sensor. On the other hand, a number of simple chromogenic or fluorogenic methods can also be used to detect aldehydes, but they have some other disadvantages such as the requirement of multiple steps to quantify the glutaraldehyde concentration [7–9].

It has long been known that liquid crystals (LCs) can be used for real-time detection of organic vapors [10–12]. For example, when some organic vapors diffuse through cholesteric LCs, the color of the LCs may change due to the change in the pitch of the cholesteric LC phase. Although these systems are simple to use, they are relatively nonselective. Any organic compounds that dissolve in the LCs may cause color changes. In contrast, orientational transitions of LC thin films supported on chemically functionalized surfaces have been successfully used to detect organic vapors with high sensitivity [13–15]. The principles of these LC-based detection systems are summarized as follows [16–20]. First, molecular receptors which weakly bind mesogens (molecules form LC phases) are immobilized on a surface, and a thin layer of LCs is spin-coated onto the surface. Then, the sample is exposed to a vaporous analyte, which can diffuse through LCs and binds to the molecular receptors on the surface. If the binding of the analyte to the receptors is stronger than the binding of the mesogens, it is able to displace mesogens from the receptors, and triggers an orientational transition of LCs. In the past, several molecular receptors and their corresponding target analytes have been identified. For example, metal ions were used to detect organophosphonates [13,14], and carboxylic acids were used to detect organoamines [15]. Although these systems have good sensitivity for organophosphonates and organoamines, the bindings of molecular receptors to target analytes are caused by noncovalent molecular interactions, such as metal–ligand coordinations or acid–base interactions. Because these noncovalent bindings are relatively nonselective, many ligands other than organophosphonates may also complex with metal ions while any strong bases can react with acids. Therefore, these systems lack the specificity to the target analytes. In contrast, the formation of covalent bonds represents a more stable and more specific interaction between receptors and the target analytes. Recently, based on the formation of covalent bonds, we

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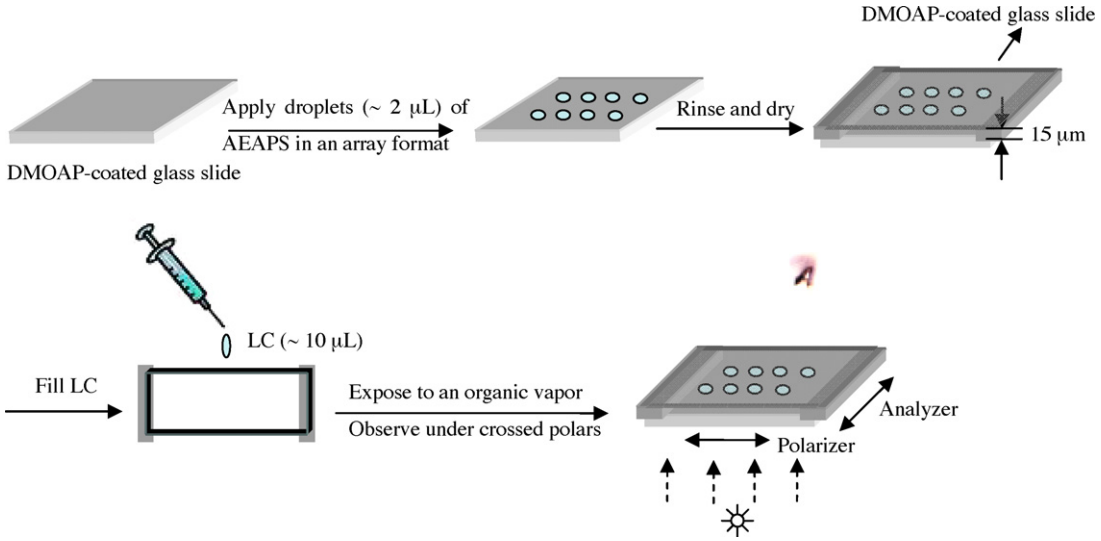

Fig. 1. Schematic illustration of surface modification and fabrication of a LC cell.

reported a principle to detect glutaraldehyde by using the surface reaction between aldehydes and primary amines [21]. Although this method shows high specificity and sensitivity for glutaraldehyde, it is an indirect method. Therefore, it cannot be used for the real-time monitoring glutaraldehyde. Herein, in an effort to improve our previous system, we design a real-time LC-based glutaraldehyde sensor by supporting a thin layer of LC on an amine-decorated surface. This new design allows the orientations of LCs respond to glutaraldehyde vapors in a real-time manner.

2. Experimental

2.1. Materials

Glass slides were obtained from Marienfeld (Germany). *N*-(2-aminoethyl)-3-(trimethoxysilyl)propylamine (AEAPS), *N*,*N*-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP), and 50% glutaraldehyde aqueous solution were purchased from Sigma–Aldrich (Singapore). Liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) was purchased from Merck (Singapore). All solvents used in this study were HPLC grades. Water was purified by using a Milli-Q system (Millipore).

2.2. Preparation of substrates

Glass slides were cleaned three times by sonicating in a 5% Decon-90 solution for 15 min. After this, they were immersed in 4 M of NaOH for 30 min, and rinsed thoroughly with deionized water. The cleaned glass slides were then immersed into an aqueous solution containing 0.1% (w/v) of DMOAP for 1 min, and rinsed with copious amounts of deionized water. The DMOAP-coated glass slides were dried under a stream of nitrogen and then heated in a 100 °C vacuum oven for 15 min to allow the crosslinking of silanol groups to form siloxane networks.

Next, we prepared two types of amine-terminated glass slides. The first type was prepared by spotting droplets (~2 μL) of AEAPS aqueous solutions (with different concentrations) onto the DMOAP-coated glass slides in an array format (Fig. 1). The glass slides were then incubated at 50 °C for 2 h in a sealed chamber to prevent the evaporation of droplets. The second type (optimal amine-terminated surface) was prepared by immersing the DMOAP-coated glass slides in 50 mM AEAPS aqueous solution at 50 °C for 2 h. Our previous results [21] showed that with the above stepwise immobilization procedures, DMOAP will occupy 50% of the surface whereas AEAPS will occupy the rest 50%. Finally, both types of glass slides were rinsed with copious amounts of deionized water and acetone to remove residual silanes followed by drying under a stream of nitrogen and heating in a 100 °C vacuum oven for 15 min.

2.3. Fabrication of LC sensors

A hybrid LC cell was made by facing two DMOAP-coated glass slides together with two strips of plastic spacer (~15 μm) and two binder clips. The bottom surface was also decorated with circular domains of AEAPS. After the LC cell was made, 5CB was drawn into the cavity formed between the two glass slides by using capillary force. After the fabrication of LC cells, they were exposed to the glutaraldehyde vapor. Copper grids were cleaned by sonicating in methanol, ethanol, and acetone sequentially for 15 min, and then heated at 100 °C overnight. These grids were then placed onto an optimal amine-terminated glass slide. Approximately 0.5 μL of 5CB was dispensed onto each grid, and excess 5CB was removed by touching 5CB with a capillary tube. Finally, the surface was exposed to glutaraldehyde vapor in a small sealed container. The optical appearances of these samples were observed by using a polarizing optical microscope (Nikon ECLIPSE LV100POL, Tokyo, Japan) in the transmission mode. Each image was captured by a digital camera (Nikon DIGITAL SIGHT DS-U1, Tokyo, Japan) mounted on the microscope with an exposure time of 25 ms.

2.4. Preparation of glutaraldehyde vapors from glutaraldehyde solutions

Glutaraldehyde vapors were prepared from glutaraldehyde aqueous solutions with different concentrations. The glutaraldehyde vapor concentration was calculated by using Henry's law (Henry's constant for glutaraldehyde is 3.3×10^{-5} L atm mol^{-1} [22]) when the glutaraldehyde concentration was below 20%. When the glutaraldehyde concentration is 50%, the experimental value of 207 ppmv was used as the vapor concentration [22].