

Construction of a Liquid Crystal Biosensor and Detection of Heavy Metal Ions and Organic Phosphate

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Abstract

Since the discovery of liquid crystal molecules have been widely used in electronic display devices. At the same time, as special "sensitive elements", liquid crystal molecules have also been introduced into the field of sensors in recent years, especially in life science research, where they have been used to for constructing liquid crystal biosensors, the first appearance. Liquid crystal biosensors are fast, simple and low-cost, label-free, highly sensitive, and with low detection limits. Therefore, the development of new liquid crystal sensors is undoubtedly a great development in the field of chemical biosensors.

Keywords

Heavy Metal Ions; Liquid Crystal; Biosensors.

1. Introduction

Liquid crystal molecules, as a new type of material, have been widely used in modern industry since their discovery, such as: watches, calculators, computers, televisions and other display devices. In recent years, liquid crystal molecules, as special "sensitive elements", have been introduced into the field of sensors, especially in life science research, for the construction of liquid crystal biosensors, opening up a new world.

2. Overview of Liquid Crystal Biosensing Methods

The basic principle of liquid crystal biosensors is based on the rapid response of liquid crystal molecules to external stimuli, whose optical response is determined by the arrangement of the liquid crystal molecules. Differences in the arrangement of the liquid crystal molecules as well as the tilt angle affect the imaging variations of the liquid crystal sensor under polarised light microscopy. Therefore, liquid crystal biosensors need target substances to directly or indirectly affect the arrangement of liquid crystal molecules, so that the presence or absence and concentration of target substances can be determined.

2.1. Liquid Crystal Molecular Properties

Liquid crystal molecules are between liquid and crystalline, a polymer ordered material, there are incomplete orientation long-range order and positional order, both liquid like fluidity, but

also similar to the anisotropy of the crystal. Its main characteristic is optical anisotropy, or birefringence, that is: natural light through the polarizer into linearly polarized light. When the linearly polarized light through the anisotropic liquid crystal, birefringence decomposition into natural light and unusual light. The direction of polarisation of natural light is perpendicular to the plane formed by its forward direction and optical axis and parallel to the direction of the wavefront. The direction of polarisation of unusual light is polarised parallel to the plane formed by its forward direction and optical axis and parallel to the direction of the wavefront.

2.2. Classification of Liquid Crystal Molecules

Liquid crystal molecules according to its arrangement is mainly divided into three kinds: nematic, smectic, cholesteric. Liquid crystal display has become a daily life must be a television set, hospitals used by the monitoring instrument, electronic watches, mobile phone screens, digital camera viewport, etc.

Nematic: meaning silk in Greek, liquid crystal molecules are arranged in parallel, with the long axis directionally ordered, and the directionally ordered distance is about thousands of angstroms.

Layer type: in Greek is the meaning of clay, liquid crystal molecules arranged in a layer structure, each molecule and the level of perpendicular or have a certain angle of inclination, so the composition of the molecules are arranged in parallel with each other, but the molecules of the interlayer interaction force is weaker, the layer and the layer can be moved to each other with a quadratic nature of the fluid, and viscous than the general liquid is notable.

Cholesterol type: liquid crystal molecules have the same layer structure as layer-type liquid crystals, but the arrangement of molecules within the layer is similar to the column type liquid crystals, the molecular long axis in the layer into a parallel arrangement, the direction of the molecular axis of each layer with the molecular axis of the neighbouring layer has a slight bias in the direction of the axis of the molecules. The liquid crystals change direction along the helix axis forming a continuous torsion and are perpendicular to the helix axis.

3. Application of Liquid Crystal Biosensors

3.1. Detection of Heavy Metal Ions

The liquid crystal molecule as a good sensitive material is based on its ability to respond to external stimuli (e.g. electric or magnetic fields) of its fast response. Moreover, due to anisotropy, an orderly arrangement of liquid crystals can be introduced by an antibody molecule or cellular disruptions. Whereas such changes in arrangement can be conveyed by optical signals, any change in the initial state is related to the nature and concentration of the introducer This is the principle behind the use of liquid crystals in biosensors.

Many environmental pollutants (e.g., pesticides, heavy metal ions) are enzyme inhibitors, and their detection can be achieved by inhibiting enzyme activity [1-3]. Based on this strategy, researchers have carried out a series of work on liquid crystal sensing. For example, Jang's group modified ten neck groups and ten MUA on the gold network, and then added the enzyme, using the reaction between the amino group of the enzyme and the completed group of MUA to modify the enzyme onto the gold network. Then 5C molecule was irradiated with UV light to make it pH responsive. When urea is added, it can be hydrolysed by the enzyme to cause the pH to rise, which causes the liquid crystal to change from horizontal to vertical alignment, and the corresponding optical appearance to change from bright to dark. When heavy metal ions are present, it can inhibit the enzyme activity and keep the liquid crystal shape unchanged. Therefore, the detection of heavy metal ions (e.g., copper ions) can be achieved by using the change of light and dark shapes.

Hu[4] at Kyungwon University, Korea, et al. modified ultraviolet (UV)-treated 5CB with urea incubation with urease, which hydrolysed urea to produce ammonia, generating NH_4^+ and OH^- , and photochemically degraded 5CB, which disrupted the LC orientation layer, showing an optical phenomenon of light to dark. On this basis, heavy metals modelled on Cu^{2+} could effectively inhibit urease activity to achieve Cu^{2+} . Cu^{2+} as a model for heavy metals can effectively inhibit the urease activity and thus achieve the detection of Cu^{2+} . When urea was in contact with the Cu^{2+} -blocking urease, there was no optical change in the LC. When ethylenediaminetetraacetic acid (EDTA) reactivated Cu^{2+} to inhibit urease, the LC orientation shifted and the optical field of view alternated between light and dark. This study can be used to accurately monitor the presence of enzyme inhibitors such as heavy metal ions.

In 2015 Singh's group[5] synthesised amphiphilic potassium N-methyl N-dodecyl dithiocarbamate (MeDTC) using Hg^{2+} chelation with MeDTC to form a rapidly stable complex leading to disruption of self-assembly to detect Hg^{2+} in tap water.

Nguyen[6] induced LC orientation by self-assembly of cetyltrimethylammonium bromide (CTAB) and used arsenic aptamer (Ars-3 aptamer) as a molecular recognition element for sensitive detection of As^{3+} in aqueous solution.

3.2. Detection of Organophosphorus

The sensing technology for OPs is maturing as organophosphorus is widely studied as a major component of chemical warfare agents and pesticides and as a potent inhibitor of acetylcholinesterase (AChE).

In 2013, Chen [7] from Tamkang University, immobilised paraoxonase 1 (PON1) on the substrate as a sensitive layer, and the product of hydrolysis of OPs. The product of hydrolysis of OPs will further dissociate and release H^+ in aqueous solution, causing a local pH decrease and thus inducing the orientation change of LCs to achieve the detection effect.

Zhou [8] from Shandong University used alkaline phosphatase (ALP) to hydrolyse DDVP. The lowest detection limit of the constructed LC sensor was $0.1 \text{ ng}\cdot\text{mL}^{-1}$.

Subsequently in 2020 Qi demonstrated the establishment of a supramolecular spherical liquid crystal sensing platform for the detection of organophosphorus pesticides[9]. Supramolecular spheres were formed by self-assembly of sodium dodecatungstophosphate (PW12), tetradecanoylcholine chloride (Myr), and polymetallic oxides (POM), which behaved in the dark state when the supramolecular spheres came into contact with the LC on the treated glass substrate, which was vertically aligned. When acetylcholinesterase (AChE) appeared, the enzyme dissolved the supramolecular spheres deposited on the surface, and the vertical orientation of LCs was destroyed, which showed a bright state. Since the presence of OPs can effectively inhibit the enzymatic action and protect the stability of the basal supramolecular spheres, the vertical orientation of LCs is stable when OPs are present, and the sensor remains in the dark state. The liquid crystal sensing platform successfully detected organophosphates with a detection limit of $0.9 \text{ ng}\cdot\text{mL}^{-1}$.

Liao [10] et al. reported the enzymatic growth of a gold nanoparticle-based of a novel acetylcholinesterase (AChE) liquid crystal biosensor. In this approach, acetylcholinesterase (AChE) mediates the hydrolysis of acetylthiocholine (ATCl) to generate thiocholine, which further AuCl_4^- reduction to gold nanoparticles. This process, known as biometallisation, leads to a greatly enhanced optical signal in the LC biosensor due to the large size of the gold nanoparticles, which greatly disrupts the orientational alignment of the liquid crystals. On the other hand, the hydrolysis of ATCl is inhibited in the presence of acetylcholine (ACh) or organophosphorus pesticides (OPs), which inhibits the catalytic growth of gold nanoparticles and thus disrupts the orientational response of LCs.

4. Conclusion

From the first curious discoveries by chemists to the current mass production of liquid crystal displays, the liquid crystal molecule has led the way in modern industrial technology. At the same time, its high sensitivity to external stimuli (electric or magnetic fields) and the high-speed development of modern integrated circuits have brought an unprecedented revolution to the electronics industry.

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