Adlayer structure innovation and film-based fluorescent sensors

1: ADLAYER STRUCTURE INNOVATION AND FILM-BASED FLUORESCENT SENSORS

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Abstract – Film-based Fluorescent Sensors (FFSs) represent a crucial option in the realm of developing high-performance sensors for dangerous, toxic, harmful chemicals, biological substances, and radioactive materials. By focusing on aspects such as mass transfer, energy transfer, microenvironment effects, and the utilization rate of sensing units that significantly impact the performance of FFSs, we elaborate on the pivotal role of adlayer structure innovation in the development of FFSs. This encompasses key areas like sensing units design and synthesis, modulation of excited state processes, and optimization of adlayer structures. Furthermore, we delve into innovations in sensor hardware structure and advancements in detection equipment. Drawing from these discussions, we explore the development prospects and major challenges facing FFSs.

Keywords: film-based fluorescent sensors (FFSs); adlayer structures; mass transfer; energy transfer; micro-environment effect

1. OVERVIEW OF FILM-BASED FLUORESCENT SENSORS

Sensors serve as the cornerstone of modern industry and digitalization, playing a crucial role in the Fourth Industrial Revolution driven by artificial intelligence and big data. Sensor technology research has gained significant importance over the years, becoming a key field in which countries worldwide are investing in and competing. However, it is important to recognize that sensor research and development require substantial investments, involve inherent risks, and often have long development cycles.

Unlike traditional gas-sensitive sensors, the key to advancing odor recognition sensors capable of rapidly and highly sensitively detecting hazardous, toxic, harmful chemicals, biological substances, and radioactive materials on-site for critical disease diagnosis lies in the development of sensitive organic thin film materials. This necessitates the rational design and precise preparation methods for creating organic structures on substrate surfaces, along with the implementation of complementary characterization techniques and strategies.

Film-based Fluorescent Sensors (FFSs) represent a cutting-edge advancement in chemical sensing technology, leveraging the sensitivity of excited states of fluorescent substances to detect microenvironment changes. In the realm of sensor innovation, FFSs offer a host of distinctive advantages, including: (1) ample room for innovation and exceptional detection sensitivity; (2) seamless device integration and effortless array formation; (3) no pollution to the testing system, enabling reusability; (4) compact dimensions, low power consumption, no need for radioactive sources, and straightforward structure, enhancing portability and versatility.

As a result of these features, research on FFSs is garnering increasing interest and is positioned as a highly promising next-generation technology for trace detection of harmful substances, following in the footsteps of ion migration spectroscopy.

The fundamental technologies underpinning FFSs primarily revolve around two key areas: (1) advanced techniques for preparing high-performance sensitive materials, and (2) sensor structures, particularly the optical system configurations of the sensors. Original research endeavors are predominantly concentrated on these critical domains. While there is limited scope for hardware structure innovation in FFSs, the primary thrust lies in the innovative fabrication of sensitive thin films.

Presently, the spotlight is on achieving selective and ultra-sensitive detection of organic compounds in the gas phase, with significant implications for public safety, environmental preservation, and human well-being. Unlike previous emphasis on inorganic elements such as NOx and SOx, the detection of such organic substances in the gas phase necessitates specialized organic structures. This poses notable challenges, including: (1) precise control over the preparation of substrate surface organic structures and optimization of sensing performance, (2) mitigation of photochemical degradation of substrate surface organic structures, and (3) autonomous design and optimization of sensor configurations. These focal points represent crucial areas of research in the realm of FFSs.

When it comes to fluorescent-sensitive thin films, their structure typically comprises substrates and sensing elements. The arrangement of sensing elements within the sensitive layer (adlayer) plays a pivotal role in determining the sensing performance and photochemical stability of the thin film. The sensing process typically unfolds through the following steps: (1) target molecules diffuse to the adlayer surface and adsorb, (2) target molecules move within the adlayer, (3) target molecules interact with excited state sensing elements in the adlayer, inducing changes in the film's fluorescence properties, and (4) target molecules desorb from the adlayer. It is evident that the type of sensing elements, substrate chemistry, substrate surface characteristics, and thin film fabrication techniques all influence the overall performance of the film. Therefore, to develop sensitive thin film materials with superior sensitivity, selectivity, and high photochemical stability, a comprehensive approach is essential. This entails focusing on various aspects such as the rational design of sensing elements, thin film preparation methodologies, and the effects of the substrate.

2. DEVELOPMENT OF FILM-BASED FLUORESCENT SENSORS

In response to challenges such as the complexity of achieving a balance between high photochemical stability, adaptability, and selectivity in sensitive materials used for detecting explosives and drugs, the monopolization of sensor structures centered around waveguide tubes, and the stringent requirements for system technology integration, stability, and weather resistance, a comprehensive research approach has been undertaken. This approach includes the design and synthesis of sensing units, innovative thin film preparation, sensor structure design, system technology integration, and equipment development.

Through dedicated efforts, an all-encompassing and distinctive thin film fluorescent sensing technology system has been created, which is distinguished by the utilization of small molecule compounds as sensing active materials and layered sensor structures. The advancements include the development of explosive single-mode, drug single-mode, and explosive/drug dual-mode detection technologies, complemented by the appropriate detection equipment.

2.1 Sensing film fabrication

Sensitive films are at the heart of FFS technology, and the innovative preparation and high-performance characteristics of these films play a crucial role in determining the advancement of FFS technology. Over the past two decades, the author's team has addressed the challenging balance between the photochemical stability and sensing performance of conventional sensitive film materials by developing various strategies for creating fluorescent sensitive films. These films are characterized by small molecule fluorescent materials and finely controlled adlayer structures.

Film Formation through Chemical Assembly：One of the key strategies employed is the formation of chemical monolayer assembly films. This involves chemically bonding polycyclic aromatic hydrocarbons to the substrate surface using flexible connecting arms. By leveraging the excited state properties of these materials and the influence of the connecting arm conformation on the microenvironment, the team has successfully developed high-performance fluorescent sensitive films for detecting explosive materials like TNT and nitroaromatic compounds such as picric acid. This approach has unveiled the "connecting arm layer shielding effect/enrichment effect." Additionally, by utilizing conjugated oligomers as sensing units and implementing surface chemical bonding, the team has achieved a synergistic effect combining the "signal amplification effect" of large conjugated units with the benefits of chemical assembly. The introduction of environment-responsive side-chain structures has further expanded the innovative space for creating chemical assembly films with conjugated oligomers as sensing units. This has led to the achievement of sensitivity and response speed records for TNT detection at the 10^{-15} mole level, enabling high-performance detection of various substances in water, including nitromethane, nitrobenzene, black powder, Octogen, and more.

Film Formation through Gel Mediation: By capitalizing on the diverse network structure characteristics of molecular gels, the team has developed highly permeable fluorescent sensitive film materials through the design and synthesis of small molecule fluorescent gelators. This approach has effectively addressed issues such as mass transfer difficulties and low utilization of sensing units commonly encountered in traditional physically coated films. The result is a significant improvement in film response speed, response reversibility, and signal-to-noise ratio, enabling high-sensitivity, high-selectivity, and rapid reversible detection of typical explosives, drug simulants, nerve agent simulants, and other substances.

Combination Design Film Formation: To address the gas-phase detection challenges posed by highly volatile liquid explosives (triacetone triperoxide, TATP, and diacetone diperoxide, DADP) and drugs, the author's team has innovatively designed and synthesized fluorescent sensing units with non-planar structures. By employing different fabrication approaches such as solution assembly, Langmuir-Blodgett (L-B) film assembly, and substrate-induced assembly, the team has successfully developed a diverse range of fluorescent sensing films enriched with "molecular channels" within the adlayer, which is expected to integrate chromatographic effects, capillary condensation, and the microenvironment sensitivity of the excited state of sensing units, enabling high-performance sensing. This strategy has facilitated successful detection of extremely challenging explosives and drugs such as "Mother of Satan" (TATP, DATP), methamphetamine, fentanyl, and more.

Film Formation through Interface-Constrained Dynamic Condensation: In response to the significant challenges posed by non-uniform film structures and the intricate control of adlayer structures due to substrate effects and "coffee ring" phenomena, the team has engineered a series of structurally complete, flexible, self-standing yet durable nanoporous films with adjustable thickness ranging from tens to hundreds of nanometers. Through the innovative approach of interface-constrained dynamic condensation and the design and synthesis of low molecular weight building blocks, these self-standing, self-healing films exhibit exceptional sensitivity and reversibility in detecting a wide range of substances including formic acid, HCl, ammonia, hydrazine hydrate, ozone, ClO_2, and more.

2.2 Hardware structure innovation

Hardware structures are necessaries for sensitive materials to showcase their full potential and become sensors with practical application value. Addressing the challenges of structural looseness, high power consumption, and difficulty in miniaturization faced by front-surface measurement systems in commercial fluorescence instruments, as well as the dominance of patented waveguide-based fluorescence measurement technologies, a novel axial arrangement of layered thin film sensor structures was developed. This innovative design includes components such as light sources, narrow-band filters, sample chambers, sensing units, broad-band filter arrays, and light signal collection units, resulting in patents being granted in both China and the United States.

Compared to commercial instruments and waveguide structures, the layered structure offers superior integration, enhanced stability, and reduced power consumption. The breakthrough in hardware structure holds significant importance for advancing the development of new FFSs and sensor arrays based on FFSs.

2.3 Development of FFSs and related detectors

By optimizing pairing of optical components, developing low-noise power supply systems, enhancing weak signal collection, and amplification circuits, utilizing layered sensor structures, and incorporating newly developed sensitive thin films, a range of high-performance explosive sensors, drug sensors, explosive/drug array sensors, and corresponding explosive single-mode, drug single-mode, and explosive/drug dual-mode detectors with fully independent intellectual property rights have been successfully engineered (refer to Figure 1). This achievement has led to the establishment of a comprehensive explosive/drug detection technology system and the inception of Shenzhen Lijian Defense Technology Co., Ltd., a specialized company focused on the research, production, and distribution of chemical sensors.

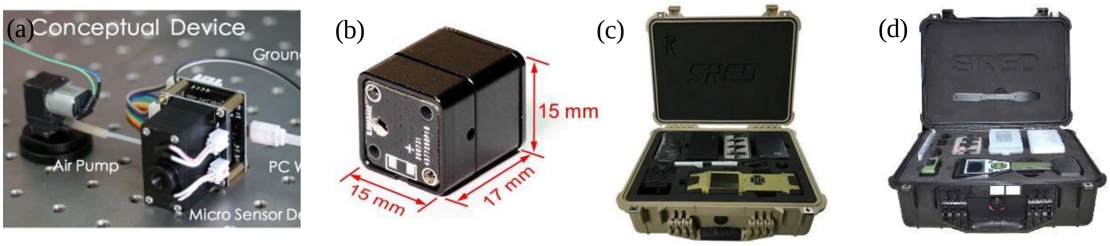

Figure 1. Examples of different types of explosive/drug sensors and various models of detectors.

Note: (a) Conceptual explosive/drug dual-function FFSs; (b) Commercial explosive FFSs; (c) FFSs-based SRED-EPI type explosive detector; (d) FFSs-based SRED-I type drug detector

3. RESEARCH PROSPECTS OF FILM-BASED FLUORESCENT SENSORS

Miniaturization, intelligence, and multi-functionalization stand out as pivotal trends in sensor development. With the emergence of FFSs, focusing on diversifying types, bolstering anti-interference capabilities, and enhancing operational stability are key areas for future advancement. It is imperative to recognize that despite the numerous advantages of FFSs, challenges such as suboptimal photochemical stability in thin-film devices, multiple interferences in sensing processes, and inconsistent sensing performance persist. Therefore, continuous efforts are essential in refining sensor unit structure design, controlling excitation state processes, advancing interface engineering, selecting optimal device fabrication methods, and improving advanced multidimensional signal acquisition and processing techniques.

Moreover, the rapid evolution and integration of artificial intelligence and big data technologies present unprecedented opportunities for sensor research, alongside imposing unparalleled demands. Essentially, research on FFSs should transcend mere detection of hazardous substances and instead actively cater to the pressing need for novel sensors in non-invasive disease diagnosis through volatolomics, as well as in remote health management. The development of FFSs technology capable of analyzing complex samples like exhaled breath, body odor, and bodily volatile compounds for wearable, real-time, in-situ, and online detection is indispensable. Consequently, the advancement of FFSs will encounter heightened challenges, necessitating integrated approaches encompassing enrichment, separation, and detection as pivotal solutions.

In conclusion, FFSs exhibit vast application potential and significant market opportunities, yet they confront substantial hurdles. Leveraging the exceptional design flexibility rooted in organic structures, the high sensitivity of sensing performance, the integrability within hardware structures, and the portability in FFSs utilization, ongoing research in FFSs will play an increasingly pivotal role in addressing major national infrastructure needs and ensuring public health security. Chemical researchers, particularly physical chemists specializing in interfacial concerns, will assume an increasingly crucial role in driving these advancements forward.

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