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Review Article

Different Approaches in Designing of Fluorescent Sensors

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ABSTRACT

Fluorescent sensors have emerged as powerful tools in analytical chemistry, enabling the detection and quantification of specific analytes or target molecules. This review provides an in-depth analysis of different approaches in designing of fluorescent sensors. It explores the selection and modification of fluorophores, the incorporation of molecular recognition elements, and the utilization of various sensing mechanisms. Research and advancements in this field continue to enhance the capabilities of fluorescent sensors, making them indispensable in various scientific disciplines and driving future developments in analytical chemistry.

Keywords: Fluorescence, Sensors, Analytical, Chemistry, Quenching, Designing

Introduction

In the past few years, there has been a significant change in sensor technology. Instead of using large and complicated transducers that take a long time to process information, the focus has shifted to using small and simple probes that have advanced capabilities and are cost-effective [1-4]. Fluorescent sensors serve as diagnostic instruments which exploit the phenomenon of fluorescence to identify and measure the presence of specific molecules or ions

in a specimen. These sensors typically incorporate a fluorescent molecule that experiences a modification in its fluorescence characteristics when in the presence of the target analyte. This adjustment may be manifested as a change in the strength, wavelength, or duration of the emitted light, and is normally translated into a numerical assessment of the concentration of the target analyte [5-7]. Numerous instances of fluorescent sensors have been designed for a range of purposes such as ecological monitoring, medical assessment, and pharmaceutical study [8]. The first step in designing fluorescent sensors is to understand the sensing mechanism, which involves determining how the target analyte interacts with the fluorescent molecule or material, leading to changes in fluorescence properties. To ensure selectivity, the sensor design incorporates molecular recognition elements such as receptors or binding sites [9-11]. Over the past few decades, there has been a significant interest in quantum dots and other innovative fluorescent nanoparticles due to their distinctive physical and chemical characteristics. These properties are primarily associated with their photophysical properties, adaptable surface chemistry, ability to bind ligands, and the potential for preservation in desired coatings or binding to different materials while maintaining their light emission properties. The effectiveness of these nanoparticles in optical sensing stems from their ability to undergo optical excitation and transfer valence layer electrons to the conduction layer. The resulting electron-hole species can be utilized through various approaches to design chemical sensors and detect different analytes. In many analytical processes, modifying the surface chemistry of nanoparticles is employed to develop sensors [12-14]. The modification of surface chemistry can occur through direct interaction with the analyte or through the interaction between the nanoparticle surface and the interface, as well as the interface and the analyte. This assay relies on the interaction between the analyte ion and the ligand or surface of the nanoparticle [15,16] In this Review, different methods used in designing fluorescent sensors have been discussed.

1. Fluorescence quenching due to analyte binding to the fluorescent nanoparticle surface

The fluorescence of the nanoparticle can be effectively quenched when the analyte ions bind to the surface ligand or functional groups. The selectivity of this assay method relies on the strong affinity between the analyte ions and the surface ligands. Various quenching mechanisms, such as internal filter effects, the creation of ion-induced non-radiative recombination pathways, and light-induced electron transfer processes, can be effective in this approach. This method is

commonly used for a wide range of cations (such as copper, mercury, silver, nickel, manganese, chromium, cadmium, cobalt, lead, and tin) [17].

2. Activation of fluorescence due to analyte binding to the fluorescent nanoparticle surface

The fluorescence of the fluorescent nanoparticle can be enhanced when the analyte binds to its surface, leading to the deactivation of traps and the removal of surface defects. This is achieved through the formation of a passive layer on the surface.[18] The removal of non-radiative relaxation pathways and the creation of additional or new radiative centers on the surface. The activation of fluorescence in nanoparticles has been utilized for the measurement of various cations, including zinc, copper, mercury, silver, cadmium, aluminum, barium, calcium, and tin [19,20]. The increase in fluorescence was attributed to the structural changes in the ammonium coating surrounding the quantum dots [21]. It was suggested that the electrostatic interaction between the analyte and the micellar coating restricts the irregular orientation of the ligand on the surface, resulting in a more uniform arrangement around the nanoparticle. This type of surface deactivation can also be achieved using certain molecules. [22]

3. Fluorescence quenching as a result of displacement of the ligand by the analyte ion

When there is a strong affinity between the ligand and the analyte ion, the ligand can be displaced from the quantum dots, leading to the formation of defects on the surface and the aggregation of nanoparticles. As the concentration of the analyte increases, the emission of the quantum dots gradually diminishes. This approach has been utilized for the measurement of arsenite [23].

4. Assay based on nanoparticle fluorescence amplification and its quenching by analyte

In this measurement method, the fluorescence enhancement approach of nanoparticles is initially employed to deactivate the surface states using an intermediate agent. Subsequently, different analytes can cause enhanced fluorescence quenching depending on their affinity for the intermediate agent. This approach, also known as the on-off method, has been reported for certain ions like copper and cadmium [24], as well as non-ionic analytes such as hydrogen peroxide [25] using quantum dots, and glutathione [26] using carbon dots.

5. Creation of selective sites on the nanoparticle for analyte fluorescence measurement in an off-on manner

In this method, which differs from the previous approach, the fluorescence of the nanoparticle is initially turned off by an intermediate agent, and then the emission intensity increases in the presence of the analyte. When the analyte is cationic, the intermediate agent is placed on the surface and serves as an ion template for the analyte. This method has been utilized for a limited number of cations, such as cadmium and zinc [27], as well as anions like cyanide, sulfide, and selenite [28,29], and numerous nonionic analytes [30–32], using various types of fluorescent nanoparticles.

6. Analyte measurement due to quencher production

In these approaches, the intermediate agent initially interacts with the nanoparticle, causing a change in its fluorescence response. Subsequently, due to its higher affinity for the analyte, the signal is turned on (or off) and returns to its initial state. Indirect measurement provides a valuable means to leverage the unique advantages of fluorescent nanomaterials as probes for measuring chemical species that do not directly affect the nanomaterials' fluorescence. Another indirect measurement method involves the use of an intermediate agent that does not directly interact with the nanoparticle. Instead, this intermediate agent reacts with the desired compound, resulting in the production of a product that alters the fluorescence response of the nanoparticle. This reaction can take various forms, such as derivatization, oxidation-reduction reactions, precipitation reactions, complex formation, and enzymatic reactions. In this method, the reactants of the reaction, with at least one being the analyte, do not have an impact on the fluorescence, while the product of the reaction modifies the fluorescence [33-40].

7. Analyte measurement by ratiometric method

To measure analyte using the ratiometric method, the concentration of the analyte is determined by comparing the emission ratios at two different wavelengths. This method requires either two fluorescent species with distinct emission wavelengths or one fluorescent species with two distinct emissions, such as different types of metal quantum dots doped with manganese or copper. By keeping one of the signals constant, an internal standard is created in this method,

which allows for internal calibration to correct for various factors that are independent of the analyte. This is an improvement compared to single-signal methods [41-45].

Conclusion

Fluorescent sensors offer a versatile and powerful approach for the detection and quantification of specific analytes. The design principles discussed in this review provide a foundation for the development of new and improved fluorescent sensors. By carefully selecting and modifying fluorophores, incorporating molecular recognition elements, and utilizing different sensing mechanisms, researchers can design sensors with enhanced performance and selectivity. With their wide range of applications, fluorescent sensors continue to play a crucial role in analytical chemistry, contributing to advancements in various fields.

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