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Inner filter effect-based fluorescent sensing systems: A review

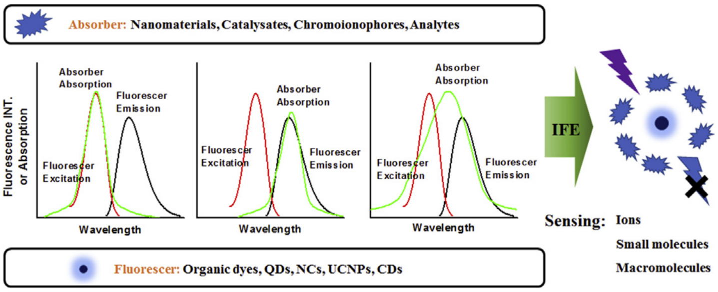
Shuai Chen [a], Yong-Liang Yu [b, *], Jian-Hua Wang [b]

[a] College of Life and Health Sciences, Northeastern University, Shenyang 110169, China
[b] Research Center for Analytical Sciences, Department of Chemistry, College of Sciences, Northeastern University, Box 332, Shenyang 110819, China

HIGHLIGHTS

- Inner filter effect in the application of sensing field.
- The fundamental, essential conditions and material option of IFE-based sensing.
- Critical applications of IFE-based sensing systems for various target analytes.
- The benefits/limitations and perspectives of IFE-based sensing.

GRAPHICAL ABSTRACT



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ABSTRACT

Inner filter effect (IFE) was previously considered as an error in fluorescence measurement. In recent years, it has been developed as an important non-irradiation energy conversion model of spectroscopic technique and found wide applications in the fields of chemical sensing and biosensing. In comparison with traditional techniques based on forster resonance energy transfer (FRET), the IFE-based fluorescent approach is more flexible and straightforward without the link of absorber with fluorescer. The present review for the first time introduces the state of the art in the progress of the IFE-based fluorescent sensing systems, including sensing strategy, essential conditions, materials option, and their applications for the detection of various target analytes, e.g., ionic species, small molecules, and macromolecules. In addition, the benefits and limitations of the IFE-based fluorescent sensing systems are also critically discussed and highlighted.

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* Corresponding author.
E-mail address: yuyl@mail.neu.edu.cn (Y.-L. Yu).

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1. Introduction

Fluorescence is a physical phenomenon described for the first time by Sir John Herschel on quinine in 1845 [1]. Fluorescent based sensing systems for chemical and biochemical analyte sensing have received much attention in recent years, owing to the benefits of excellent sensitivity, favorable selectivity, operational simplicity, real-time detection, and portability. Various fluorescent sensing methods [2,3] based on a fluorescence quenching process have been designed and developed, including static quenching effect (SQE), dynamic quenching effect (DQE), and photo-induced electron transfer (PET), forster resonance energy transfer (FRET), electronic energy transfer (EET), surface energy transfer (SET), and intramolecular charge transfer (ICT). However, the design of analyte recognition probe is complicated, because the probe must be specifically sensitive to the analyte and with good fluorescence properties at the meantime. Although various energy-transfer sensing systems can solve this problem by separation of donor and acceptor, in practice the construction of this type of fluorescent sensors with ideal stability is often complicated and extraordinarily time-consuming in order to keep a proper distance between the donor and the acceptor.

Inner filter effect (IFE) is an important non-irradiation energy conversion model in spectrofluorometry, which results from the absorption of the excitation and/or emission light by the absorber in the detection system [4]. In the past, IFE became a problem for any fluorescence measurement, especially when an absorbing component was titrated into the cuvette [5]. However, since the changes in the absorbance of absorber translate into exponential changes in the fluorescence of fluorescer, an enhanced sensitivity and decreased detection limit for the analytical method is obtained with respect to the absorbance alone [6–8]. Yang et al. firstly designed a highly selective fluorescent sensor for the detection of copper(II) ion based on an IFE of the UV–visible absorption of a spiropyran derivative on the fluorescence of a metal porphyrin [9]. It offers a feasibility to convert a classic colorimetric protocol into a fluorescence sensing approach, simply based on an IFE, to overcome its inherent shortcomings, e.g., inferior detection sensitivity, poor repeatability, and/or complicated interfering factors.

In recent years, plenty of literature have reported the superiority and application of novel IFE-based sensing techniques. As a new sensing field, we hereby summarize the current status of the IFE-based sensing systems and their applications in a comprehensive way. Firstly, a general introduction of IFE-based sensing is presented. Following that, the mechanisms of IFE, sensing strategy, and essential conditions are discussed. An emphasis is also put on the materials that are currently available in the IFE-based analysis. The applications of the IFE-based sensing have covered a broad range of analytes, including ionic species, small molecules, and macromolecules. Finally, the current challenges and future prospects of the IFE-based fluorescent sensing assays are discussed.

2. General sensing mechanisms and strategy

2.1. IFE basics

IFE has been observed by Stokes [10]. It is found that blue fluorescent of concentrated quinine comes only from the solution surface irradiated by ultraviolet light. It is because that the quinine solution is relatively concentrated and absorbs all of the ultraviolet light in the first several millimeters. After passing through the solution, the light is “enfeebled” and could no longer excite quinine to produce blue glow. However, the fluorescence decreasing phenomenon is hardly observed in the low optical density solution. The fluorescence intensity of a sample containing a mixture of non-interacting fluorescers is simply the sum of their respective contributions. Since the observed fluorescence intensity is proportional to the intensity of the excitation light, the apparent quantum yield is somewhat less than that observed for an infinitely dilute solution. This is called an inner filter effect. IFE may decrease the intensity of the excitation at the point of observation, or decrease the observed fluorescence due to the light absorption. This absorption of excitation and/or emission radiation by a sample matrix reduces the fluorescence intensity and results in a nonlinear relationship between the observed fluorescence intensity and the concentration of fluorescer.

Commonly, IFE is considered as a source of error in fluorometric analysis, and investigators attempt to restore the linear relationship between the fluorescence intensity of fluorescer and its concentration by avoiding the IFE. Due to the absorption of excitation or emission light, attenuations are sometimes called the primary or secondary inner filter effect. Primary inner filter effect (pIFE) refers to the absorption of excitation radiation by various chromophores in solution or matrix, and secondary inner filter effect (sIFE) relates to the absorption of emission radiation by these same chromophores. Sir George found that the fluorescein solution with a longer absorption wavelength than quinine would have still been excited by the “enfeebled” light. It is because that each IFE process depends upon the optical densities of the sample at the excitation and emission wavelengths [10]. In practical analysis, sIFE can be avoided completely if an emission wavelength is used where no component in the sample absorbs light. However, IFE can be minimized or even be ignored but cannot be eliminated completely, because absorption by fluorescer must occur to provide the excitation. Moreover, IFE is rather obvious in many practical situations. Therefore, some attempts have been made to compensate for the inner filter and to