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Original article

Recent advances in fluorescence sensor for the detection of peroxide explosives

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ABSTRACT

The detection of peroxide explosives (PEs) has attracted considerable attention all over the world in global security owing to their simple preparation, poor chemical stability and easy decomposition. In recent years, great efforts have been devoted to developing organic fluorescence sensors for detecting the PEs because of their fast response, high sensitivity and high selectivity. In this short review, we firstly discuss the sensing mechanisms for fluorescence based the PEs detection. Next, we reviewed recent progress of PE probes in the nearly 5 years and the design strategies of the material structures to enhance the sensitivity or selectivity, such as conjugated polymers and assembled nanoparticles.

1. Introduction

In recent decades, peroxide explosives (PEs) are becoming more and more noticeable as one class of the most elusive explosives to individual health [1,2], social stability [3] and terrorism activities [4]. From hydrogen peroxide (H_2O_2) to organic peroxides (Table 1), such as triacetone triperoxide (TATP), diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD), which can be easily made from commercially available precursors (H_2O_2, an acid, and acetone). TATP is one of the most sensitive explosives known, which has 88% explosive equivalence of TNT [5]. Well-known terrorist attacks using TATP as bombs including Richard Reid's shoe bombing on December 22, 2001 [6], the London bombings on July 7, 2005 [7], and the suicide bombers on the evening of 13th November 2015 in Paris and the explosions at the airport and the metro station in Brussels on Tuesday 2th March 2016 [8]. H_2O_2 is considered as an intrinsic impurity, which can be generated via UV decomposition or simply leaking of the PEs [9]. It's worth noting that the mixtures of H_2O_2 and alcohols or acetone can be used as powerful explosives as well [10]. Thus, trace the detection of H_2O_2 vapor is crucial for security scenarios [11].

The first method for quantitative trace analysis of peroxide-based explosives is described by Karst et al. [12] using reversed-phase high-performance liquid chromatography method with postcolumn UV irradiation and fluorescence detection for the analysis. After that, there are various methods and successful technologies used to report about detection the PEs, such as the electrochemical [13–16], voltammetric [17,18], electrogenerated chemiluminescence (ECL) [19,20], spectrophotometry [21,22], thermodynamic [23], differential scanning calorimetry (DSC) and thermogravimetric analyzer (TG) [24], high-performance liquid chromatography [25,26], mass spectrometry (MS) and ion mobility spectrometry (IMS) [27–29] and so on. In spite of several presented methods of sensing PEs, they generally needed large instrument, a complex pretreated process, long operation time, and low sensitivity [30]. As a contrast, fluorescent technique is a current efficient method with simplicity, high sensitivity, selectivity and fast response to explosive detection [31,32].

Compared to nitroaromatic explosives, e.g. 2,4,6-trinitrotoluene (TNT), the PEs are extremely difficult to detect by conventional techniques owing to their lack of UV–vis absorbance, fluorescence, a nitro group, or facile ionization that can benefit intermolecular $\pi-\pi$ stacking interactions with electron-rich chromophores. Moreover, sensitivity to mechanical stress, easily decomposition

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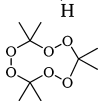
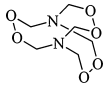
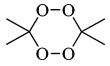
Table 1
Compounds of interest for explosive detection [33].

Structure	name	abbreviation	P_{vap}, 25 °C/Torr
	Hydrogen peroxide	H_2O_2	2.05×10^{-1} [a]
	Triacetone triperoxide	TATP	4.65×10^{-2}
	Hexamethylene triperoxide diamine	HMTD	[b]
	Diacetone diperoxide	DADP	1.33×10^{-1}

p/Torr. 1 Torr = 133.322 Pa = 1.3158×10^{-3} atm; 1 Pa = 7.5006×10^{-3} Tor r= 9.8692 10^{-6} atm; 1 atm = 760 Torr = 760 mmHg = 101.325 kPa.
[a] The HP (aq.) concentration used can vary from 3% up to ca. 60%.
[b] No vapor pressure data for HMTD were reported, instead a number of decomposition products were observed.

and so on also makes the sensing of the PEs more challenging. In this short review, we will discuss the sensing mechanisms of fluorescence based the PEs detection, summarize recent progress on the fluorescence probes in the nearly 5 years, and list the design strategies of the material structures to enhance the sensitivity or selectivity.

2. Signal mechanisms

As mentioned above, fluorescence-based explosives detection is an indirect method which utilizes the interaction of fluorescent sensory materials and explosive to trigger a fluorescence signal change, and hence detects the presence of the explosive.

There are several fluorescent phenomena generated by the concentration and exposure time of explosives in the sensing process, such as intensity (quenching or enhancement), wavelength, or lifetime. In this review, the following parts summarized three kinds of sensing mechanisms commonly used for PEs probe design.

2.1. Boronate oxidation reaction

Among all the reported fluorescent PEs probes, the probe based on boronate oxidation reaction dominates. Chemical reaction between the boronate group and H_2O_2 results in obvious fluorescence changes due to the transformation of the molecule structure. The high selectivity of the boronate oxidation reaction has been recognized by previous studies [34].

H_2O_2 possesses ambiphilic reactivity. On the one hand, its labile O–O bond allows it to react as a two-electron electrophilic oxidant. On the other hand, because of the α-effect of adjacent nonbonding orbitals on its oxygen atoms makes H_2O_2 be a good nucleophile [35,36].

Upon reaction with H_2O_2, aryl boronates act as an electrophile in a reversible manner with nucleophiles to form a negatively charged tetrahedral boronate complex. After that, the C–B bond becomes reactive as a nucleophile (Fig. 1). The reaction of masked boronates with H_2O_2 is released to form aromatic phenols as functional groups. To improve the efficiency of these characteristic molecular features, we could utilize this dual-mode complementary ambiphilic reactivity of H_2O_2 with boronates to achieve sensitivity and selectivity, so that this single reaction could endow a plenty variety of fluorescent molecules to realize the detection of H_2O_2.

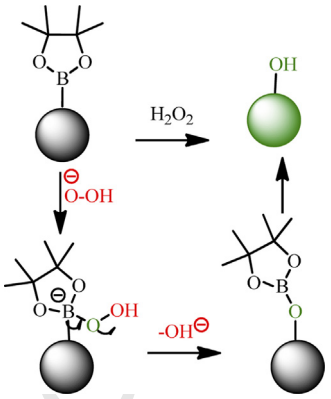


Fig. 1. The sensing mechanism of boronates as fluorescent probe to detect H_2O_2.

2.2. Specific aldehyde oxidation reaction

Recently, our group [37] designed a highly efficient multi-formyl phenol/amine system for fluorescence detection of H_2O_2 vapor (Fig. 2.). The hydroxyl group together with three formyl units was used to construct a donor–π–acceptor fluorescent molecular probe. Then, the hydroxyl group of the probe reacted with diethylamine to form the ionized molecule. Experimentally, the aldehyde groups of the ionized molecule were either partially or completely oxidized to obtain the carboxylic phenol upon reaction with PEs vapor. Furthermore, the oxidized carboxylic products could form H_2O_2-related multiple hydrogen bonds, the intermolecular H-bonding interactions is beneficial for a more efficient adsorption capacity H_2O_2 vapor, which boost response speed, and enhance sensitivity.

The sensing mechanism is far better than that of boronate oxidation reaction mechanism in PEs sensing whatever in sensitivity or response rate. It also provided a new prospective method to design more efficient PEs vapor sensors *via* utilizing a reaction product to strengthen the interaction between the object analyte and the sensing material.

2.3. Sulfoxide profluorophores

Unlike previously described mechanisms, a special strategy was proposed by Malashikhin et al. [38] using aromatic sulfoxide reagents for visible fluorescence detection of nmol-quantities of TATP. The aromatic sulfoxide fluorophore emission was modulated by the oxidation of an adjacent heteroatom.

Sulfones **1c**-**3c** was more fluorescent than the corresponding sulfoxides, which provided an opportunity for oxidation-based visual TATP detection (Fig. 3). For example, a 50-fold emission increase of **3c** relative to **3b** was observed and could be easily discerned by naked eye. A visual response to as little as 100 nmol of TATP could be generated after 90 min. Fluorescent signaling based on sulfoxide profluorophore only required brief photolysis, and it

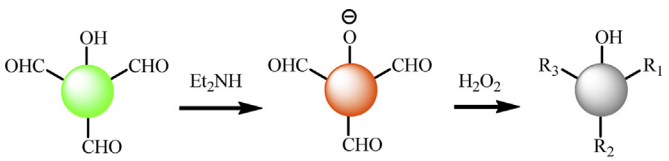


Fig. 2. The sensing process of multi-formyl phenol–amine system as fluorescent probe to detect H_2O_2.

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