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Highly sensitive colorimetric paper sensor for methyl isothiocyanate (MITC): Using its toxicological reaction

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ABSTRACT

Highly sensitive and portable sensors are tools to improve personal protection from exposures to unwanted toxic chemicals. A paper-based colorimetric sensor was designed and prepared to sensitively and selectively detect trace amounts of methyl isothiocyanate (MITC) in the air. Taking advantage of a detoxification reaction existing in the mammalian body, glutathione (GSH) becomes unique in indirectly sensing the concentration of methyl isothiocyanate. The reaction mechanism was analyzed, and the detection conditions were optimized. Nanofibrous membrane materials were utilized as a solid substrate with ultrahigh surface areas. An organic polar solvent with high adsorptive capacity to MITC was applied on the fiber surfaces. A combination of three factors drives the detection of traces toxic gas in air kinetically favorable.

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1. Introduction

Fumigants are a group of agricultural toxic volatile organic compounds (VOCs) that are commonly applied as pre-planting pesticides in agricultural production [1,2]. Methyl isothiocyanate (MITC), has been developed as an effective alternative fumigant of methyl bromide, and the application of MITC shows a noticeable increment in recent years [1,2]. Moreover, MITC is the major metabolite and active component of other effective fumigants like sodium methylaminomethanedithioate (metam-sodium) and 3,5-dimethyl-1,3,5-thiadiazinane-2-thione (dazomet) [1]. Multiple routes of MITC emissions increase the risk of over-exposure to MITC in the environment. Because of the acute toxicity of MITC, the permissible exposure limit (PEL) of MITC is reported as 270 ppb [3]. The high vapor pressure of MITC makes it readily diffuse from the soil to the atmosphere, causing a serious risk to farm workers and residents who live nearby [1]. Therefore, the development of a rapid and easy detection of the toxic gas could be an option of reductions of unwanted exposure to the toxic vapors. Traditional detection methods like gas chromatography coupled with different detectors can accurately qualify and quantify the presence of different fumigants in the environment [4–7]. The complex sample collection, extraction, and preparation, as well as a high cost of the instruments are the major drawbacks of instrument detections.

Sensors for toxic gases have been developed, such as those based on electrical signals [8,9], color [10–13], biological signals [14,15] and other factors [16,17]. Among them, the variance of color in colorimetric sensors makes the detection of target compounds, like VOCs be observed by naked eyes. For instance, Yoon and coworkers selectively sensed four VOCs based on color changes of polydiacetylenes [10]. Lin et al. designed a preoxidation technique to highly improve the detection sensitivity of VOCs on a colorimetric sensor array [11]. Moreover, Liu et. al., and Zhao et. al., developed different conjugated polymer systems to selectively detect volatile amines in the vapor phase [18,19]. Meanwhile, highly sensitive sensors for detection of gas pollutions such as CO, NO_x and NH_3 can also be found [8,20,21]. More specifically, the detection methods for MITC can also be found in literatures. Headspace-SPME was designed for MITC sampling, and GS-MS–MS was incorporated in detection [22]. Noguer, T., et al. [23] reported a disposable monoenzymatic biosensor to detect MITC at 100 ppb in aqueous solution, but it does not show any application results for MITC vapor. More efforts were focusing on detection of MITC with non-portable instruments [24].

Glutathione (GSH), a tripeptide that widely exists in mammalian cells, is famous for its detoxification mechanism [25–28]. Researchers have demonstrated that the formation of conjugates with glutathione in animal cells is one of the metabolic processes of electrophilic toxicants. GSH is a soft nucleophile because of the presence of a thiol group, and it readily reacts with electrophiles such as halogenated alkyls, unsaturated ketones under a physiological condition with the assistance of glutathione-S-

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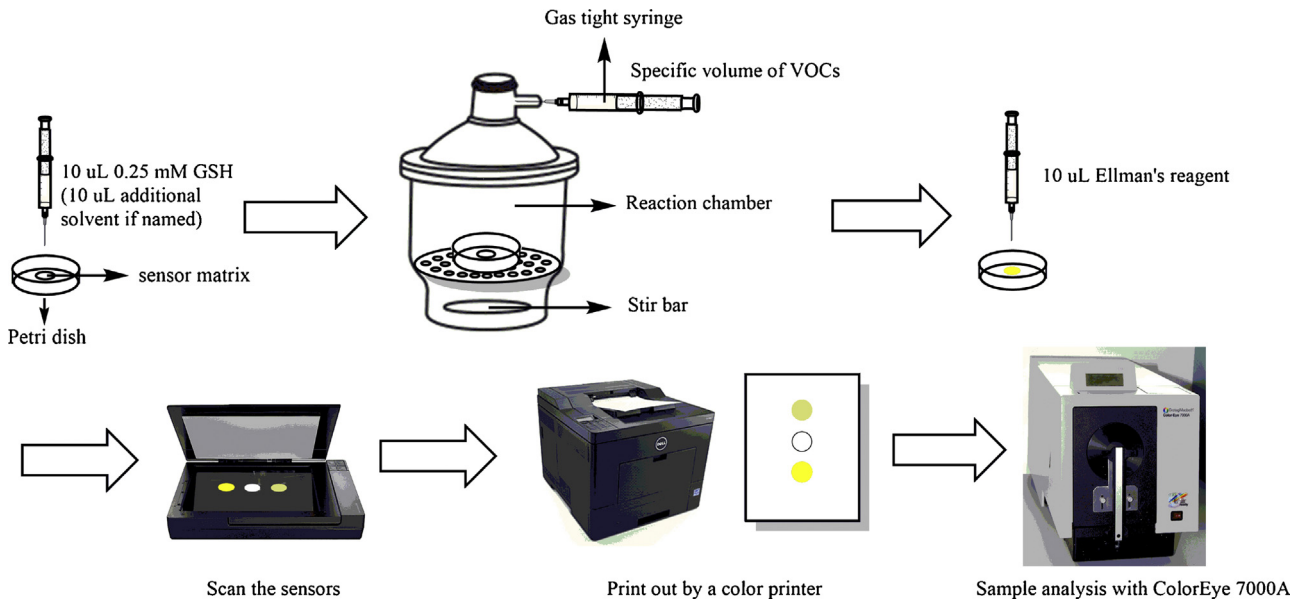

Fig. 1. Experiment setup of MITC detection sensor.

transferase [29–31]. The metabolism of fumigants working with GSH is determined by their electrophilicity. Methyl isothiocyanate (MITC) ( ) contains an electron deficient carbon connecting to a nitrogen and a sulfur atom, which could react with GSH, resulting in detoxification [29]. According to the GSH detoxification reaction of MITC, a colorimetric sensor can be designed and developed to quantify the residual GSH, by using the Ellman's reagent (5,5′-dithiobis-(2-nitrobenzoic acid) or DTNB), forming a yellow ion (TNB^{2-}) after reacting with the thiol groups in the residual GSH [32].

In the present study, the development of a highly sensitive colorimetric paper sensor has been described. The discussions will focus on the combination of three strategies 1) reaction condition adjustments, 2) the selection of nanofibrous membrane as a sensor matrix, and 3) the application of MITC interactive solvent for creating a kinetically favored detection environment on the surfaces of the fibers. The reaction mechanism was investigated with UV–vis spectroscopy and ^{13}C nuclear magnetic resonance (^{13}C NMR). The concentration of MITC in the air is inversely proportional to the depth of yellow color showing on the sensors after applying Ellman's reagent. Reaction pH, an addition of an organic solvent, and ultrahigh surface sensor paper media served as key factors to maximize the sensitivity and selectivity of the sensor, as well as driving the reaction to be kinetically favorable and achievable on the special paper-based media.

2. Experiments

2.1. Materials and chemicals

Reduced glutathione, monobasic sodium phosphate monohydrate (MSP), sodium hydroxide, and all organic solvents used in this study were purchased from Fischer Scientific Co. (New Jersey, USA). Methyl isothiocyanate (MITC) was bought from ARCOS Organics (New Jersey, USA). Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ellman's reagent (5,5′-dithiobis-(2-nitrobenzoic acid) or DTNB) was bought from Thermo Fisher Scientific Co. (Waltham, MA, USA). All chemicals are analytical grade and were directly used as received.

Whatman™ wet strengthened cellulose filter papers (CF) and glass microfiber filters (GMF) were bought from GE Healthcare Life Science (Pittsburgh, PA, USA). Silicon dioxide nanofibrous membrane (SNF) was provided by Donghua University, China. The preparation procedures of the SNF were described in details in literatures [33,34].

2.2. Sensor setup and detection procedures

Sensor matrixes were cut into circular shape with a radius r = 3.0 mm. Reduced glutathione (GSH) was dissolved in monobasic sodium phosphate (MSP) aqueous buffer (0.1 M MSP and 1 mM EDTA). EDTA was added to the buffer to avoid oxidation of glutathione by heavy metal ions. The pH value of the buffer was adjusted with 10 M NaOH. Each sensor was wet with a selected organic solvent and 10 μL of 0.25 mM GSH solution before putting into a gas chamber. Then, a specific volume of fumigant solution was directly injected into the gas chamber. The conversion of fumigant volume from target concentration was calculated with Eq. S1 and more detailed information on the preparation of fumigant samples in various concentrations are listed in Table S1. The chamber was well sealed, and the sensor was exposed to different concentrations of MITC for specific durations. After that, Ellman's reagent (5,5′-dithiobis-(2-nitrobenzoic acid) or DTNB) (4 mg/mL in MSP buffer, pH = 8.0) was dropped onto the sensor to visually detect residual GSH by showing different depths of yellow color. Fumigants are highly volatile toxic gases, so all sensing procedures were run in a fume hood. The yellow color and corresponding color changes shown up on the paper sensors are visible by naked eyes. In the designed sensor system, the color intensity represents the residual concentration of free thiol groups and an inverse order of MITC concentrations in air chambers.

Since the faint yellow color difference resulted from the Ellman's reagent is hard to be read precisely by naked eyes, to obtain numerical results of the color difference employed in the investigation, colors on the paper sensors were scanned with an Epson Perfection V33 scanner (Epson America, Inc., Long Beach, CA, USA) and then was printed out with a Dell 2150chn color printer (Dell Inc., Round Rock, TX, USA). The thus obtained yellow colors on the sensor were measured with a GretagMacbeth ColorEye 7000A colorimeter (Akron, Ohio, USA) according to color coordinates L^*, a^* and b^*. L^*

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