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Equipment-free chromatic determination of formaldehyde by utilizing pararosaniline-functionalized cellulose nanofibrous membranes

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ABSTRACT

Determination of environmental contaminants such as trace formaldehyde mostly relies on bulky and costly analytical equipment. However, a particular demand for portable, rapid, and sensitive method that can be used in resource-limited settings has received paramount concern. Towards this need, we are presenting here a rational design of colorimetric sensor strips using electrospun cellulose nanofibrous membrane-immobilized pararosaniline. Based on the specific reaction between formaldehyde and pararosaniline, the strips could undergo a distinct color transition from light pink to purple, specifically in the presence of trace-level formaldehyde over other possible interferential volatile organic compounds. Benefiting from the large specific surface area and high porosity of nanofibrous membranes, the strips achieved ultralow naked eye detection limit of 0.06 mg m^{-3} (below the regulatory level of 0.1 mg m^{-3}), wide linear range from 0.12 to 6 mg m^{-3}, and short response time (15 min) in the absence of advanced instrumentation. Additionally, the sensing responses were visualized quantitatively by HSI coordinates which are presented with lightness and chromatic values and analyzed by a principal component analysis method. Furthermore, the strips exhibited remarkably improved analytical performance compared to commercial filter paper-based ones. With its cost-effective design and portability, this sensitive and specific colorimetric strips could potentially be used for providing air contamination information.

1. Introduction

There is an urgent demand for rapid, sensitive, accurate, and portable determination of toxic volatile organic compounds (VOCs), not only from a security perspective, but also for use in the chemical workplace [1,2]. As one of the most commonly used chemicals, formaldehyde has drawn substantial concern in the past and nowadays as well since it can vastly affect different systems within living organisms and even cause cancer [3,4]. These findings have added weight on the severity of formaldehyde, thus the World Health Organization (WHO) has set a guideline value of 0.1 mg m^{-3} averaged over 30 min for formaldehyde in virtue of its acute toxicity [5].

Thus far, although commonly used techniques such as chromatography, quartz crystal microbalance, fluorescence, and chemiluminescence could be applied to detect formaldehyde at parts per billion levels, the sophisticated equipment, complex manipulation, or long analysis time have limited their widespread application [6–10]. Considering the drawbacks of the aforementioned techniques, there is a critical need for a rapid approach to verify trace concentration of formaldehyde. As low-cost alternatives, colorimetric sensors are uniquely promising because of diversely favored features including easy-to-use, portable, and fast response [11–13]. Further, colorimetric detection could be a convenient way to realize assay for qualitative results as well as quantitative analysis of target molecules by measuring the absorbance intensities of the colorimetric reaction [14–16]. To date, numerous colorimetric sensors have been developed to detect formaldehyde, for instance, chromotropic acid assay, pH indicators, and nanoporous pigment detection [17–19]. However, these colorimetric sensors suffer from several limitations: it is difficult to detect

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compounds at low concentrations relative to their vapor pressures, and the discrimination between compounds within a similar chemical class is limited. These consequences might be caused by the small specific surface area (SSA) and porosity of sensors' substrates (quartz, filter paper, porous glass, and silica gel). Therefore, there is an obvious pressing need for a substrate with ideal structural characteristics to circumvent those limitations and realize a faster and more sensitive detection of formaldehyde.

Electrospinning has steadily garnered popularity predominantly due to the promising applications of electrospun nanofibrous membranes in nanoscience and nanotechnology over recent decades [20–22]. The three-dimensional (3D) structured fibrous membranes are assembled by the electrospun fibers with controllable pore structure and SSA. The advantageous properties such as large specific surface area, high porosity, and spatial interconnectivity enable the nanofibrous membranes to be implemented in the field of sensors [23,24]. Cellulose nanofibrous membranes are counted as one of valuable platforms for probe immobilization owing to the striking features like excellent hydrophilicity, ease of functionalization, and porous structure.

In this contribution, we provide a sensitive, selective, and cost-effective method for gaseous formaldehyde assaying by integrating electrospun cellulose nanofibrous membranes with pararosaniline (PAR). To the best of our knowledge, no effort has been spent to develop formaldehyde sensors based on the fact that formaldehyde could specifically react with pararosaniline labeled on nanofibrous membranes. Benefiting from the large SSA and high porosity of the nanofibrous membranes, the as-prepared strips achieved an extremely low naked eye detection limit of 0.06 mg m^{-3}, and the color discrimination comes close in magnitude to allow for naked eye recognition. Moreover, the sensing performance of the colorimetric strips has been systematically investigated at room temperature and analyzed by a principal component analysis (PCA) method. With its cost-effective design and field portability, this sensitive, reversible, stable, specific, and fast-response colorimetric strips could be potentially exploited to determine gaseous formaldehyde.

2. Experimental

2.1. Materials

Cellulose acetate (CA) with the acetyl content of 39.8% (M_w = 30,000) was purchased from Sigma Aldrich Inc., USA. PAR (biological stain grade), formaldehyde (gas chromatography grade), and acetaldehyde (gas chromatography grade) were obtained from the Aladdin Reagent Co., Ltd., China, sodium sulfite, sodium hydroxide, hydrochloric acid, *N*,*N*-dimethylacetamide (DMAc), acetone, and other VOCs were all analytical grade and provided by Shanghai Chemical Reagent Co., Ltd., China. Ultrapure water with a resistance of 18.2 MΩ was prepared by using a Heal-Force system. Filter paper was supplied by Hangzhou Special Paper Co., Ltd., China. All reagents were used as-received without any further purification.

2.2. Fabrication of cellulose fibrous membranes

Typically, a 15% CA precursor solution was prepared by dissolving 3 g of CA powder in 17 g of acetone–DMAc mixture (weight ratio of 1/2) with stirring for 12 h. Then, the electrospinning process was performed by using the DXES-1 spinning equipment (Shanghai Oriental Flying Nanotechnology Co. Ltd., China) with a feed rate of 0.5 mL h^{-1}, a tip-to-collector distance of 15 cm, and a high voltage of 16 kV. The electrospinning chamber was kept at the constant temperature (25 °C) and relative humidity (45%). The CA nanofibrous membranes were deposited on the paper-covered grounded metallic rotating roller and dried in vacuum at 80 °C for 2 h to remove solvent. Subsequently, the obtained fibrous membranes were hydrolyzed in a 0.05 M sodium hydroxide solution at ambient temperature for 4 days following our previous report [25]. The fibrous membranes were then washed to neutral and dried at 80 °C for 4 h to obtain the white cellulose fibrous membranes.

2.3. Preparation of colorimetric strips

The probe solution was prepared by mixing equal volume of the 0.02% PAR solution with 0.1% sodium sulfite solution. The PAR solution was prepared and stored at 4 °C, and addition of sodium sulfite to PAR prior to storage is not recommended for its instability [26]. The colorimetric strips were fabricated by dipping a piece of cellulose fibrous membranes (1 cm × 1 cm) in the probe solution (30 mL) for 1 min at ambient temperature and then removed from the solution, as shown in Fig. 1. In addition, the filter paper-based strips were prepared through the aforementioned procedure for the purpose of comparing the sensing performance of strips based on different substrates.

2.4. Detection of formaldehyde

In order to detect formaldehyde accurately, the colorimetric strips were hung up in a testing chamber (9.42 L) filled under constant temperature (25 °C) and relative humidity (60%). The controlled humidity environment was achieved by using water injections into the chamber and high-purity N_2 purging through the chamber, which yielded the required humidity. A fan was applied to accelerate the evaporation of the water droplet suspended at the tip of the needle. A microliter syringe (Shanghai Anting Microliter Syringe Co., China) was used for analyte (formaldehyde and other VOCs) injections and the concentration of the evaporated analytes in the chamber was calculated in mg m^{-3} according to the following formula:

$$C = \frac{1000 w \rho V_s}{V} \tag{1}$$

where w is the injected analyte concentration in %, ρ is the density of the analyte in g mL^{-1}, V_s is the volume of the analyte in μL, and V is the chamber volume in L. The typical sensing experiment was performed as follows: the strips were exposed to formaldehyde of concentrations ranging from 0 to 6 mg m^{-3} at room temperature for 15 min. After that, the absorption spectra and images of the strips were recorded and analyzed. To investigate the

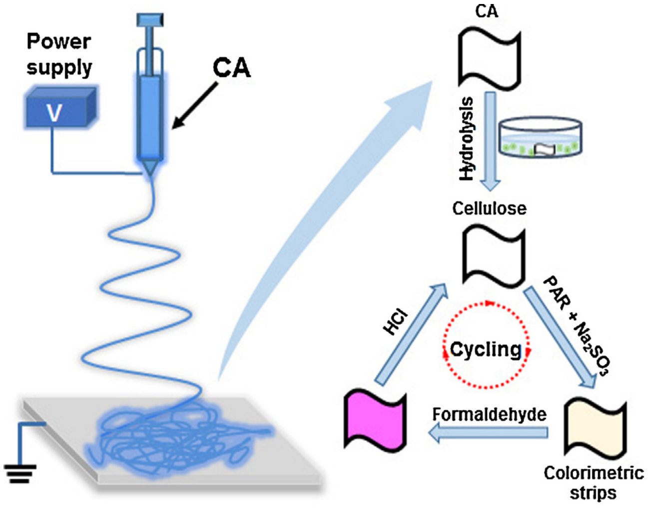

Fig. 1. Schematic illustration of the fabrication of colorimetric strips.