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A facile and highly sensitive colorimetric sensor for the detection of formaldehyde based on electro-spinning/netting nano-fiber/nets

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ABSTRACT

A novel strategy for highly sensitive colorimetric detection of gaseous formaldehyde was developed based on Methyl Yellow-impregnated electro-spinning/netting (ESN) nylon 6 nano-fiber/nets (NFN). The sensor presented a significant reflectance intensity decreasing band at 550 nm which induce the visual color changes from yellow to red after exposure to formaldehyde and allowed for the detection of formaldehyde with a low detection limit of 50 ppb. Upon exposure to a series of volatile organic compounds (VOCs), only formaldehyde could induce a yellow-to-red color change observable by the naked eye, which clearly exhibited that Methyl Yellow-impregnated nylon 6 NFN membranes could act as highly selective and sensitive strips to detect formaldehyde with minor interference from other VOCs. Additionally, the colorimetric sensor showed good reproducibility under cyclic sensing experiments. Furthermore, the colorimetric responses were visualized quantitative by using a color-differentiation map prepared form converted RGB (red, green and blue) values. As-prepared Methyl Yellow-impregnated nylon 6 NFN sensor strips successfully combined with the visualized detection of color map and fascinating structure of NFN membranes, which indicated promising composite materials as a simple and economical alternative to replace the traditional formaldehyde sensors and facilitated the design and development of other label-free colorimetric sensors toward various analytes based on the NFN template.

1. Introduction

Formaldehyde is widely used as a base chemical material to manufacture building materials and numerous household products in many industrial processes with approximately ten megatons produced per year [1,2]. However, formaldehyde is a hazardous air pollutant and prolonged exposure to formaldehyde can cause serious health effects such as central nervous system damage, immune system disorders, as well as asthma and nasopharyngeal cancer [2,3]. The exploitation of highly efficient sensors for the detection of formaldehyde continues to be a significant scientific endeavor due to its possible threat to public health [4–6]. The World Health Organization (WHO) has set a standard for safe exposure of 80 ppb averaged over 30 min [7,8]. Conventionally, an ultrasensitive detection can be achieved by identifying the output optical [9–11], electrochemical [3,12] or conducting [7,13] signals upon exposure to formaldehyde. Despite the progress, further development of current efficient sensing element is hampered by limitations of involving complex handling procedures or suffering from easy contamination, high cost, and a lack of portability.

To overcome these limitations and achieve widespread routine use, the colorimetric sensor array system, which are discovered by Suslick and co-workers, is of particularly appealing due to its effectiveness, simplicity, low cost and allows assays to be detected with the naked eye [14,15]. Up to now, numerous formaldehyde-induced color changes of sensors that are composed of arrays of metalloporphyrins [16,17], pH indicators [8,18,19], chromotropic acid [20], nanoporous matrices doped with Fluoral-P [21] and nanoporous pigments [9,10] have been successfully designed to detect formaldehyde with high selectivity. However, current colorimetric sensors for formaldehyde often use polymer film [8], cellulose tape [18,19] or even glass [22] as platform for immobilization of colorimetric sensing elements, which will inevitably cause generally relatively slow response and frequently lack sensitivity. Therefore, it is urgent to explore other general platforms to meet these challenges.

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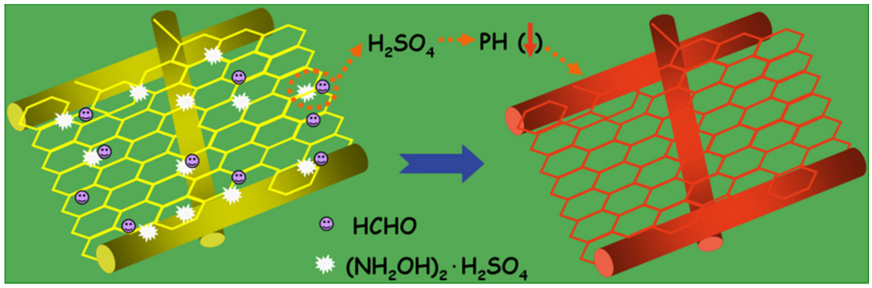

Fig. 1. Illustration of the colorimetric detection of formaldehyde based on the nylon 6 NFN membranes.

Owing to the exciting optical and structural properties, nanostructure materials have evoked much interest as attractive building blocks for sensors. As a newly discovered nanoarchitecture, NFN membrane that comprising common electrospun nanofibers and two-dimensional (2D) spider-web-like nano-nets, has risen as a shining star in the horizon on the path of the scientists' searching for new materials. So far, a lot of polymers, such as polyacrylic acid [23,24], nylon 6 [23,25,26], poly(vinyl alcohol) [27], polyurethane [26,28], polyethylene oxide [29], gelatin [30] and *Bombyx mori* silk [31] have been prepared into NFN structures. NFN membranes possess the general properties and functions of conventional electrospun nanofibers as well as the attractive features (e.g. extremely small diameter, high porosity, Steiner tree network geometry, controllable coverage rate) that distinguish themselves from their counterparts [25,32,33], which bring ESN NFN membranes highly attractive to some special area, such as ultra-fine filters to intercept viruses. More over, taking advantages of comparatively large surface area and high porosity, nano-nets can create enhanced interconnectivity and additional surface area and facilitate the diffusion of analytes into the NFN membranes and thus attractive candidates as sensing materials or template materials loaded with sensing materials for ultrasensitive sensors [34–36].

Although our previous works have revealed the formation feasibility of nylon 6 NFN structure, the further exploitation of such nano-scaled structure in facile and highly sensitive sensors is still a challenging problem and of great interest. We have very recently developed a new strategy for label-free colorimetric and specific detection of Cu(II) ions based on polyaniline/nylon 6 NFN membranes, opening new opportunities for the development of extended NFN structures in colorimetric sensing application [32]. Given our interest in the further design of novel and facile colorimetric gas sensors, here we focused on the preparation of label-free colorimetric sensor strips for the detection of formaldehyde based on nylon 6 NFN platform, which impregnated with the processing solution containing hydroxylamine sulfate, Methyl Yellow (pH 2.9–4.0, red-yellow), glycerin and methanol. When the sensor strip was exposed to formaldehyde, the Methyl Yellow on the tape reacted with sulfuric acid produced by the reaction of hydroxylamine sulfate with formaldehyde to produce a yellow-to-red color change (Fig. 1) [18]. The degree of color change could be recorded by measuring the intensity of reflecting light (550 nm). This novel sensor strip not only maintains the high surface area and porosity of NFN structure, but also effectively improves the reflectance signal. Moreover, the general approach can be used to design other label-free colorimetric sensors to detect a wide range of analytes.

2. Experimental

2.1. Materials

Nylon 6 (M_n = 18,000) was purchased from UBE Industries Ltd., Japan. Formaldehyde (GCS grade), hydroxylamine sulfate, Methyl Yellow, glycerin and methanol (analytical grade) were purchased from Aladdin Chemical Co., China. Formic acid, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and other volatile organic compounds (VOCs) (analytical grade) were purchased from Shanghai Chemical Reagents Co., Ltd. MilliQ water with a resistance of 18.2 MΩ was obtained from a Millipore system.

2.2. Fabrication of the Methyl Yellow-impregnated nylon 6 colorimetric NFN membranes

A typically procedure for fabrication of the nylon 6 NFN membranes is depicted in Fig. 2. A 15 wt% nylon 6 solution was prepared in formic acid with an ultrasonic treatment of 20 min. The resulting viscous solution was transferred into a syringe and injected through a metal needle that was connected to a high-voltage supply (DW-P303-1ACD8, Tianjin Dongwen High Voltage Co., China). The solution was fed at a constant and controllable rate of 0.9 mL/h by using a syringe pump (LSP02-1B, Baoding Longer Precision Pump

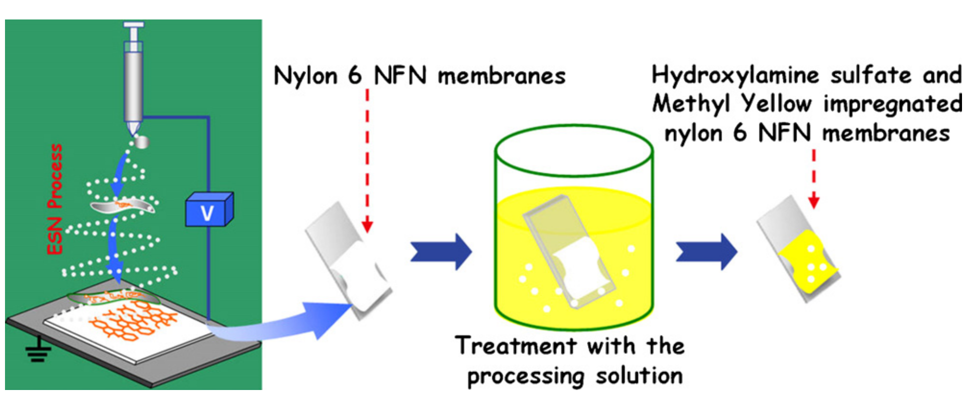

Fig. 2. Representation of the preparation of the Methyl Yellow-impregnated nylon 6 colorimetric NFN membranes.