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# Sensitive naked-eye detection of gaseous ammonia based on dye-impregnated nanoporous polyacrylonitrile mats

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ABSTRACT

Herein, highly sensitive colorimetric detection of gaseous ammonia is reported based on bromocresol green–impregnated polyacrylonitrile (BCG–PAN) nanofibers. The sensing layer with a porous nanofibrous structure was prepared simply by drop-casting a BCG solution containing polyethylene glycol (PEG) and oxalic acid on an electrospun PAN mat. The nanofiber mat exhibited durable structural stability under various conditions of acid, base, acetone and hot water. A smooth nanoporous structure of the sensor provided better color uniformity with a brighter reflectance than the porous paper, thus providing an ideal medium for high-quality colorimetric detection. Upon exposure to 25 ppm ammonia, the yellow BCG–PAN mat quickly changed and became saturated to blue within 1 min. The sensor was confirmed to have a detection limit of less than 1 ppm in the detection by the naked eyes, good selectivity to common volatile organic solvents and reversible color change behavior at ambient conditions. These results straightforwardly demonstrate that sensitive and reversible $NH_3$ detection is possible simply by observing the sensor color without the help of any detecting instruments. The addition of water-soluble PEG into a BCG solution was found to enhance sensor response probably due to its strong hydrophilicity, while the oxalic acid prevented BCG dye from deprotonating by the ambient humidity. Based on the change in reflection spectrum and a great response to amine compounds, the colorimetric detection mechanism was proposed to be the transform of BCG acid form to the base counterpart through the acid-base reaction with basic analytes dissolved into the water-containing nanofiber matrix.



## 1. Introduction

Ammonia is a hazardous air pollutant and is emitted from various artificial sources such as nitrogenous fertilizers, domestic animals, combustion, and the chemical industry [1]. The Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit of 35 ppm for the 15 min-weighted average $NH_3$ concentration in ambient air since prolonged exposure can cause acute poisoning to humans. In addition, exposure to above 300 ppm is known to be immediately dangerous to human health. The maximum concentration of $NH_3$ is stringently regulated by legislation in many countries due to its toxicity. Thus, sensitive detection of gaseous ammonia is of great significance in environmental monitoring and industrial process control. Up to now, there has been much effort to produce $NH_3$ sensors with high performance for use in a variety of application fields where it is difficult to use conventional analytical instruments. A variety of $NH_3$ gas sensors have been developed using different transducing principles based on electrical conductance [2–5], mass change [6,7], electrochemistry [8,9], and optical phenomena [10–12]. However, although some of these sensors achieve highly sensitive and selective detection, the need of additional instrumentations still limit their widespread use in application such as on-site user testing.

The colorimetric detection by the naked eyes is the simplest gas-sensing platform because there is no need for the transducing component. The sensing element in colorimetric sensors is usually made of chemochromic dyes that produce color change upon exposure to gas analyte in either reflected or absorbed light. For obtaining a sensitive and reliable colorimetric sensor, the dyes have to be homogeneously distributed and durably immobilized within a supporting medium. Although doped conducting polymers, quantum dots and metalloporphyrins have been

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**Table 1**
Properties and sensing performances of colorimetric $NH_3$ gas sensors reported in the literature.

| Dye/matrix | Detection type | Detection limit | Response time | Recovery time | Refs. |
|---|---|---|---|---|---|
| BPB/PMMA plastic film | Waveguide | <0.25 ppm | ~1 h | Several hours | [11] |
| Polyaniline/filter paper | Naked eyes | 100 ppm | 5 min | Recovered by HCl | [13] |
| BPB/PVB plastic film | Absorption | <3 ppm | 38 s ($t_{90}$) | 14 min ($t_{90}$) | [16] |
| BCG/Al-MCM-41 silica[a] | Absorption | 0.185 ppm[b] | ~2.5 min ($t_{90}$) | Recovered by heat | [20] |
| BCG/SBA-15 silica[c] | Naked eyes | <5 ppm | 1 min[d] | Recovered by heat | [21] |
| BCG/anodized aluminum | Reflectance | 1 pp[e] | 6 min ($t_{90}$) | 4 min ($t_{50}$) | [23] |
| BCG/cellulose acetate film | Reflectance | <6 ppm | 5 min ($t_{90}$) | n.a. | [24] |
| BCG/PAN nanofibers mat | Naked eyes | <1 ppm | ~1 min ($t_{90}$)[f] | 22 min ($t_{90}$) | This work |

BPB: bromophenol blue, PVB: polyvinylbutyral, PMMA: polymethylmetacrylate.
[a] Pellet.
[b] Evaluated by $3\sigma$.
[c] Detector tube type.
[d] Measured at 50 ppm.
[e] Corresponding to 10% response.
[f] Measured at 25 ppm.

introduced in colorimetric $NH_3$ detection [13–15], pH indicators are commonly used due to their low cost, easy availability and reliable halochromism. A considerable number of investigations have been performed to find an ideal supporting matrix for the halochromic dyes, including plastic films [11,16,17], silicate sol–gel [18,19], mesoporous silica [20,21], anodized alumina [22,23], and acetate cellulose films [24]. The plastic and acetate cellulose films usually contain plasticizer components to improve their mechanical properties. However, these materials generally suffer from ageing so that the sensor response shows a considerable time-dependent variation. On the other hand, the sol–gel or silica supports encounter other difficulties in fabricating a low cost sensor, as with litmus paper, despite of their enhanced durability and long-term stability. The sol–gel process often requires delicate experimental conditions and a long gel formation time while it is still difficult to form a reliable film consisting of mesoporous silica particles. Finally, the nanoporous anodized alumina prepared by electrochemical processes is innately more fragile than the organic counterparts. This drawback results in a difficulty to produce a reliable low-coat sensor in mass quantity, which limits their prevalent use despite the development of promising $NH_3$ gas sensors. To break through the hurdle, the study on a novel matrix for immobilizing halochromic dyes is still challenging. Representative characteristics and performances of the developed ammonia sensors are summarized in Table 1.

In recent years, electrospun nanofibers have attached great attention as the matrix holding gasochromic sites in colorimetric sensors [25–29]. A nanofibrous structure provides favorable gas-sensing conditions such as a high surface to volume ratio, excessive porosity, and uniform dye absorbance. These unique properties provide opportunity to fulfill the requirements desired in colorimetric detection such as a high sensitivity, short detection time, and uniform color change. Ding's group recently reported two different electrospun mats consisting of enaminone-modified polyacrylonitrile (PAN) nanofibers [28] and pH indicator-impregnated nylon nano-fiber/nets [29] for the colorimetric detection of gaseous formaldehyde vapor. The highly sensitive naked eye detections were demonstrated up to the detection limit of 40 ppb, exhibiting the benefit of nanofibrous structures. To the best of our knowledge, there have been no previous works on colorimetric $NH_3$ gas sensors using nanofiber membranes.

Here, simple pH indicator-impregnated PAN nanofiber mats were prepared for the highly sensitive, reversible detection of basic ammonia gas. The PAN matrix was chosen due to its high chemical stability, mechanical durability, and facile electrospinning [30,31]. A yellow acid form of bromocresol green (BCG), which is known as an efficient dye in $NH_3$ detection due to its appropriate $pK_a$ value [19], was used as the pH indicator and the initial color was regulated by adding non-volatile oxalic acid. The BCG-impregnated PAN (BCG–PAN) nanofiber mat was attached onto a polyester (PES) lamination film with the aid of a low-cost office laminator to improve the soft and fluffy characteristics of the mat. The resultant BCG–PAN/PES is more user-friendly and can be directly utilized as an $NH_3$-sensing unit similar to litmus paper. In this work, our colorimetric sensors demonstrated a high sensitivity (the naked eye detection of obvious greenish blue coloration even at 1 ppm), excellent selectivity to common volatile organic solvents (VOCs), and a fast detection time ($t_{90} \cong 1$ min at 25 ppm) for $NH_3$ gas detection. These performances demonstrate that the simple BCG–PAN layer can be utilize as an $NH_3$-mornitoring sensor in the important concentration range of 1–35 ppm without any additional transducing parts. Considering the sensitivity improvement via quantitative optical detection using an instrument, the detection limit of 1 ppm in the naked eye mode seems to be comparable or better than those of the developed $NH_3$ sensors listed in Table 1. Furthermore, the response kinetic, reversibility, and humidity effect were also investigated in order to clarify the sensing mechanism.

## 2. Experiment

### 2.1. Materials

PAN ($M_w$ = 150,000 g/mol), PEG ($M_n$ = 400), *N*,*N*-dimethylformamide (DMF, anhydrous), oxalic acid, acetonitrile, chloroform and methylamine (anhydrous gas) were purchased from Sigma–Aldrich. Regent-grade ethanol, benzene, dichloromethane (DCM), ethylenediamine, and BCG were bought from Daejung (South Korea). The other solvents including acetic acid, acetone, dimethyl sulfoxide (DMSO), formaldehyde, and toluene were procured from Junsei. All chemicals were used as received without further purification. Standard 50 and 1000 ppm $NH_3$ gas samples, dry air, and nitrogen were utilized in the sensing experiment. Chromatography paper (Grade 1, Whatman) and a PES lamination film were used in the sensor fabrication.

### 2.2. Fabrication of BCG–PAN nanofiber sensors

The process flow diagram of the fabrication of the BCG–PAN/PES sensor is as followings. First, a 9.1 wt% PAN solution was prepared by dissolving 1.90 g PAN powder in 20 mL DMF under stirring for 12 h at room temperature. Next, electrospinning was performed to produce nanofibers. The resultant homogeneous solution was loaded into a plastic syringe with a 20 gauge metal needle. Typically, a high voltage of 26 kV was applied to the needle using a power supply (ES30P, Gamma High Voltage), and the electrospinning solution was supplied at a flow rate of 1 mL $h^{-1}$ by a syringe pump (NE-1000,