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Original article

Detection of ammonia based on a novel fluorescent artificial nose and pattern recognition



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ARTICLE INFO

Article history:

Received 28 July 2015

Received in revised form

25 October 2015

Accepted 25 October 2015

Available online 20 November 2015

Keywords:

Fluorescent artificial nose

Toxic gas

Cross-responsive mechanism

Artificial neural network

Ammonia

ABSTRACT

A simple and rapid fluorescent sensor array for identification and quantification of different concentrations (ppb level) of ammonia was proposed in this paper. Employing porphyrin, porphyrin derivative and chemically responsive dyes as the sensing elements, the developed sensor array of artificial nose showed a unique pattern of fluorescence changes upon its exposure to ammonia for just 4 min. And the eigenvalues from raw fluorescence spectra were analyzed by means of pattern recognition algorithm, including hierarchical cluster analysis (HCA), principal component analysis (PCA) and back-propagation neural network (BPNN). The results showed that HCA and PCA, which were used to assess the feasibility and effectiveness of discrimination of fluorescent sensor array, revealed a distinct separation between samples. BPNN were used for automatically classifying and predicting concentration of ammonia, and the accuracy was 97.55% while the relative standard deviation (RSD) was up to 3.67% for real samples. It indicates the fluorescent artificial nose system is a rapid and feasible sensing platform for the identification and quantitative analysis of gases, and also shows the possibilities in the field of environmental gas detection and environmental gas monitoring.

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1. Introduction

Although ammonia is used in many important fields, such as fertilizers, refrigeration, dyes, drugs, explosives, it is one kind of industrial toxic gases, which can bring environment pollution and health hazards to human body directly or indirectly. With the increasing awareness of environmental protection, rapid detection of low-concentration ammonia remains a challenge. In addition to optical absorption detection (Peeters et al., 2000; Mount et al., 2002; PR China. Ministry of Environmental Protection, 2009), which is often used as a standard method and the operation is quite

complex, there are two main strategies for detecting gases currently. One is traditional large instruments, such as Gas Chromatography (GC), Mass Spectrometer (MS), and so on, and it is not suitable for on-site detection and is not family-oriented because of poor portability and the high cost of initial investment and ongoing maintenance. The other is based on gas sensors. A number of principles and techniques have been employed to measure ammonia, including metal-oxide sensors (Du et al., 2007; Samotaev et al., 2013; DeMeo et al., 2014), graphene-based sensors (Yavari et al., 2012; Hu et al., 2014), conducting polymer detectors (Kondawar et al., 2012; Zhong et al., 2013), electrochemical sensors (Ji et al., 2007), semiconductor sensors (Khuspe et al., 2013; Fu, 2014), surface acoustic wave (SAW) sensors (Chen et al., 2013; Tang et al., 2014; Wang et al., 2015), field effect transistor sensors (Lu et al., 2011; Yu et al., 2012; Li et al., 2013), and quartz crystal microbalance sensors (Jia et al., 2014; Li et al., 2014; Ogimoto et al., 2015). These approaches have been used successfully in chemical

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

analysis, and continued research efforts are needed to improve the accuracy and reliability.

As a new sensor array method developed by Rakow and Suslick (2000) in recent years, the colorimetric approach has been diffusely adopted in view of the excellent performance on molecular recognition. The colorimetric sensor array are widely used for odor recognition (Lim et al., 2009), molecular recognition (Suslick et al., 2010; Hou et al., 2013), and even complex mixture identification (Bang et al., 2008; Musto et al., 2009; Wu et al., 2014). These sensor arrays, which are based on cross-response mechanism and have characteristics of non-specific recognition, are characterized by imitation of smell or taste in view of a variety of sensitive elements and optimizing their combinations, and then achieve the distinguishing between targets. Therefore, they are possible to avoid the conventional sensors which have highly requirements in specific sensitive element, and have been widely used. In addition, more and more attentions are paid to fluorescence sensor recently due to its high sensitivity. Mayr et al. (2003) proposed a fluorescent cross-reactive array in a micro titer plate and succeed in predicting the presence of metal ions. Thete et al. (2009) used a fluorescent microarray based on hydrogel and achieved the characterization of liquid analytes. Xu et al. (2013) presented a fluorescence sensor for the detection of CO₂. More and more reports have indicated that the fluorescence sensor array has high specificity and sensitivity in discrimination of various kinds of analytes (Kang et al., 2014; Liu and Bonizzoni, 2014; Xu et al., 2014). Besides detecting metal ions and liquids, it can also detect gases. Therefore, unlike these principles and techniques for measuring ammonia mentioned above, which mainly depend on single signals, in this paper, based on the cross-response mechanism, a novel rapid and effective artificial nose with fluorescent sensor array for detecting low concentrations of NH₃ was proposed and realized.

2. Experimental methods

2.1. Fluorescent sensor array

The fluorescent sensor array consisted of seven chemical materials with fluorescent effect as the sensing elements, including porphyrin (H₂TTP), porphyrin derivative (TTPS), metalloporphyrin (ZnTTP), zinc porphyrin dimer (ZnPD) and three chemically responsive dyes, which were prepared according to our previous report (Fa et al., 2009; Hou et al., 2011). These kinds of materials can identify interactions between molecules such as π - π molecular complex action, bond formation, acid–base interactions, physical adsorption, and van der waals forces (Suslick et al., 2004). When interacting with specific gases that had the ability to cause the changes of the fluorescent and photochemical properties of several of the sensing elements, the fluorescence of these elements would change. Owing to this, the sensor array could show a unique responsive characteristic spectrum as the fluorescent fingerprint, which was obtained from the emission spectrums of the array before and after exposing the sensor array to gas.

In addition, the porous matrix can serve as a preconcentrator, and improve the sensitivity of colorimetric sensor array for detection of vapors. Therefore, solgel method was employed to obtain the nano-porous sensing elements. Firstly, a quartz capillary with capability of delivering approximately 0.1 μ L of solution was used to print the sensor array onto the surface of the polyvinylidene difluoride (PVDF, [CH₂CF₂]_n) membrane (pore size: 0.45 μ m; thickness: 165 μ m), which was purchased from Millipore Co., Ltd. (Billerica, USA). And then, the sensor array was placed in a 50 °C thermostat for 48 h. After that, it was kept in the dark environment under the protection of nitrogen until used. The structure of the fluorescent cross-responsive sensor array is illustrated in Fig. 1.

There were a total 21 (7 \times 3) spots on the sensor array, for each kind of element had three spots as the parallel sample to reduce negative effects.

2.2. Application of as-prepared fluorescent artificial nose for NH₃ detection

A fully utility fluorescent artificial nose for NH₃ detection was constructed, and the schematic diagram is shown in Fig. 1. It is divided into three parts: gas generator equipment, gas detection equipment (including fluorescent sensor array) and control and data processing system. The gas generator equipment is used to store and mix up N₂ and analyte. The gas detection equipment mainly consisted of a reaction chamber, excitation light source and a micro-spectrometer (purchased from Ocean Optics Co., Ltd.). An array of fluorescent artificial nose was placed in the reaction chamber for detecting different concentrations of NH₃. The excitation light source was provided by two laser diodes (LDs) of which the wavelengths were respectively 420 nm and 470 nm. Control and data processing system was composed of a personal computer and required software developed by our lab, and it not only sent commands and received signals, but also was in charge of the resources allocation, signal processing, and drawing conclusion. In addition, the auxiliary components comprised a waste cylinder for collecting the exhaust gas, a pump applied to control the flow rate of the gas stream, and other necessary hardware.

To eliminate the interference of air and other gases, it was essential to clean the whole gas path by using pure nitrogen before the detection. The two LDs alternated, turned on and off and parallel translation of the sensor array were both driven by stepper motors, and the micro spectrometer could respectively collect the fluorescence spectra of each spots at the two different excitation wavelengths. Consequently the 'initial' fluorescence spectrum was obtained before reaction. Then, gas streams containing the vapor of interest were generated by mixing the analyte and pure nitrogen. Meanwhile the concentrations of gas streams were determined by gas chromatography (GC) analysis. In the same way as the 'initial' one, the 'final' fluorescence spectrum was acquired after a certain reaction time, depending on how long the response signal of sensor array tends to stabilize. The changes of fluorescence spectra of each sensing element on the array were generated by subtracting the 'final' spectrum from the 'initial' one, and these changes could be used as a specific fingerprint of different analyte.

2.3. Data processing method

The flow chart of data analysis was shown in Fig. 2. The arithmetic average value of the 'initial' and 'final' fluorescence spectra was from three parallel sample spots of each chemical material. Then, the difference spectrum of fluorescence of each sensing element was obtained by 'initial' fluorescence spectrum minus 'final' one. Two different wavelength of LDs were used as excitation source. Accordingly a total of 14 (7 \times 2) feature points were obtained from one target, and they were recorded as X₁ to X₁₄. Due to the influence of analyte, there were some subtle differences between the excitation spectra detected by the micro spectrometer before and after the exposing. Therefore, it was necessary to remove the excitation spectral range from X_i and retain only the fluorescence spectral range. Besides a threshold *T*, which was adjustable in the analysis software, was set. If the absolute value of the fluorescence spectrum intensity was less than *T*, it would be set to zero. So far, the raw difference spectra data, feature points X₁ to X₁₄, were converted to the data which could be used to extract characteristic indexes, and they were denoted by Y₁ to Y₁₄.

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