Industrial Gases Identification Using Graphene-based Gas Sensors: NH_3 and PH_3 as an Example

Shirong Huang
Institute for Materials Science and
Max Bergmann Center for Biomaterials
TU Dresden
Dresden, Germany
shirong.huang@tu-dresden.de

Alexander Croy
Institute for Physical Chemistry
Friedrich Schiller University Jena
Jena, Germany
alexander.croy@uni-jena.de

Luis Antonio Panes-Ruiz
Institute for Materials Science and
Max Bergmann Center for Biomaterials
TU Dresden
Dresden, Germany
luis_antonio.panes_ruiz@tu-dresden.de

Vyacheslav Khavrus
SmartNanotubes Technologies GmbH
Freital, Germany
khavrus@smart-nanotubes.com

Bergoi Ibarlucea
Institute for Materials Science and
Max Bergmann Center for Biomaterials
TU Dresden
Dresden, Germany
bergoi.ibarlucea@tu-dresden.de

Gianaurelio Cuniberti
Institute for Materials Science and
Max Bergmann Center for Biomaterials
TU Dresden
Dresden, Germany
gianaurelio.cuniberti@tu-dresden.de

***Abstract*—Both ammonia (NH_3) and phosphine (PH_3) play a significant role in an extensive range of industrial processes, while they are harmful to human health even at very low concentration. So far, a variety of gas sensors have been developed to detect them in an industrial environment aimed to protect the health of workers at their work place. Among various types of gas sensors, chemiresistive type gas sensors have attracted considerable interest due to its characteristics, such as simple fabrication, high sensitivity, high reliability, etc. Nevertheless, there are still some limitations, such as, high power consumption resulted from high operating temperatures, and most sensors are solely dedicated to an individual gas monitoring. In this work, we present the development of highly sensitive and highly discriminative graphene-based gas sensors for gas detection and identification at room temperature. Graphene is exfoliated by a liquid phase approach and functionalized by copper phthalocyanine derivate (CuPc). Leveraging machine learning techniques, graphene-based gas sensors demonstrate an excellent gas identification performance towards NH_3 and PH_3 at an ultralow concentration (ppb level). This work could pave the path to design highly sensitive and smart gas sensors for a wide range of gases.**

***Keywords*—Smart gas sensors, gas identification, ammonia, phosphine**

I. Introduction

In the past decades, various types of gas sensors have been developed for both NH_3 and PH_3 detection, respectively. [1-4] Despite of the remarkable progress of gas sensing technology, the state-of-the-art gas sensors still exhibit some limitations. For instance, a high operating temperature is essential for most commercial gas sensors,. Most commercial gas sensors, such as metal-oxide-semiconductor (MOS) types, usually work at an high temperature range (e.g., 200–500 °C) due to that the thermal energy is indispensable to activate the adsorption of ionized oxygen species as well as to overcome the energy barrier of sensing reactions. [5] Furthermore, most gas sensors are generally dedicated to only one gas detection task under a pre-specified condition. For example, in order to monitor the NH_3 gas leak in an industrial environment, a specific gas sensor devoted to NH_3 detection has to be deployed; to monitor the PH_3 gas in the same workplace, a second gas sensor devoted to PH_3 detection is required. To the best of our knowledge, very few gas sensors are capable to discriminate or identify multiple industrial gases in the same environment.

In this work, we present the development of copper phthalocyanine derivate functionalized graphene-based gas sensors. Each analyte gas is represented by a feature vector containing multiple transient features extracted from the sensing response profile of a single sensor after analyte exposure. This strategy is distinct from the conventional electronic nose (e-nose) technology, which typically employs steady features (e.g., maximum response value, S) from a sensor array consisting of multiple sensors. With supervised machine learning, the developed graphene nanosensor demonstrates an excellent gas identification performance towards NH_3 and PH_3 at an ultralow concentration (ppb level).

II. Results and Discussions

Herein, we analyzed the sensing response of graphene-based gas sensors towards industrial gases, NH_3 and PH_3. Following the sensing signal data acquisition, time-domain current data were converted to time-domain sensing response signals, as shown in Figure 1 (a). Each individual measurement contains two stages, the analyte gas exposure phase (15 mins) and the analyte gas flushing phase (10 mins). To classify each gas, multiple transient features are extracted from the sensing response profile to represent each gas, as schemed in Figure 1 (b).

The typical procedure of feature extraction was as follows: firstly, the time-domain current signal was transformed into the time-domain resistance data according to Ohm's law. Then, the resistance profile was split up into 24 individual measurement profiles. Next, the fractional change of sensor resistance was derived and the sensing response profile was acquired. Subsequently, data normalization was carried out by the L_2 norm algorithm, which aimed to compensate for sample-to-sample variations in concentration. Afterwards, both response profiles in the analyte gas exposure phase (t_1-t_2) and analyte gas flushing phase (t_2-t_3) were fitted with exponential functions. Three coefficients (a_1, b_1, c_1) were obtained from the analyte gas exposure fitting curve and three coefficients (a_2, b_2, c_2) were acquired from the analyte gas flushing curve, respectively. Meanwhile, calculations of the first derivative and the second derivative of the response profile as a function of time were conducted after fitting with a polynomial function, from which both the maximum value (k_{max}) and the minimum value (k_{min}) of the first derivative of the response profile were acquired, as well as the minimum value (a_{min}) of the second

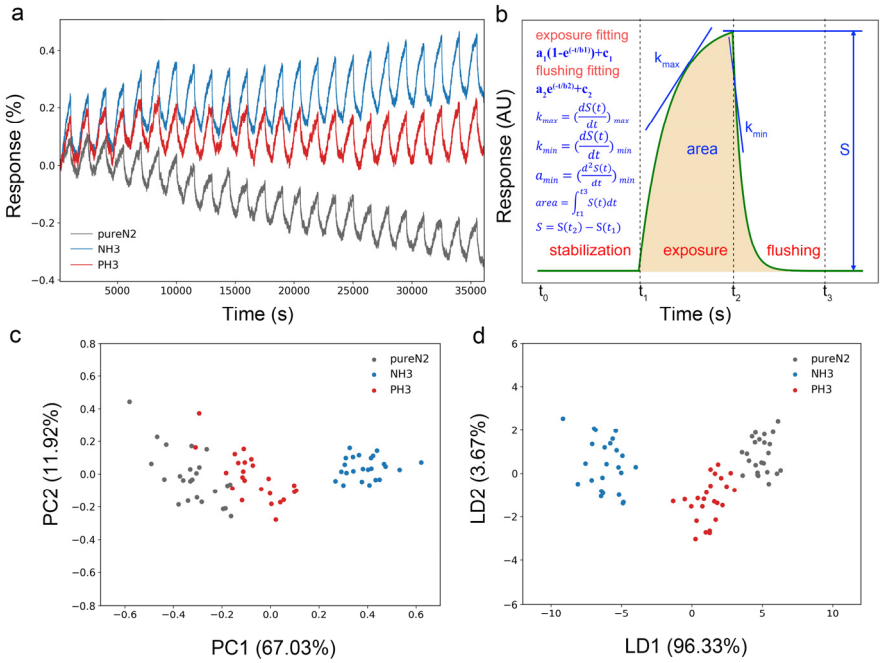

Figure 1. (a) Typical sensing response profile of graphene-based gas sensor towards 500 ppb analyte gases under cyclic testing. A complete test is composed of 24 repetitions test. (b) Schematic of sensing response profile *S(t)* of a single measurement, consisting of analyte exposure phase (t_1-t_2, 15 min) and analyte flushing phase (t_2-t_3, 10 min). The feature vector representing each analyte gas consists of 11 parameters, including, a_1, b_1, c_1, a_2, b_2, c_2, S, k_{max}, k_{min}, a_{min}, $area$. (c) PCA score plot of analyte gases at 500 ppb concentration. (d) LDA score plot of analytes gases at 500 ppb concentration. Adapted with permission from [6].

derivative of the response profile was determined, respectively. Together, the transient response S in the whole exposure phase (t_1-t_2) was calculated, as well as the area under the whole response profile (t_1-t_3) was integrated. Finally, each analyte gas was represented by a feature vector containing 11 transient features, which consisted of 24 arrays of 11 features.

All these feature data of analyte gases were then analyzed by unsupervised machine learning (Principal Component Analysis, PCA) model as well as a supervised machine learning (e.g., Linear Discriminant Analysis, LDA) model. As shown in Figure 1 (c), the first principal component explains 67.03% of the variance, while the second principal components explain 11.92%. Together, the first two principal components explain 78.95% of the variance. As can be seen in the scatter plot, NH_3 clusters are located on the right side, PH_3 clusters are located in the middle, and reference gas cluster is located on the left side. Obviously, PH_3 clusters are close to the reference gas cluster, while NH_3 clusters are far away from the reference gas cluster, suggesting that the NH_3 analyte induces a more discriminative signal than PH_3 upon interacting with functionalized graphene on the sensor. Employing supervised machining learning models, the classification results of both NH_3 and PH_3 from the reference gas (pure N_2) were achieved, for instance, using the LDA classifier, as depicted in Figure 1 (d). In contrast to the PCA algorithm, the LDA algorithm attempts to find a feature subspace that optimizes class separability. As it is shown in Figure 1 (d), NH_3 forms an isolated cluster while the PH_3 cluster approaches the reference gas cluster at 500 ppb concentration. In order to evaluate the prediction accuracy of the supervised machine learning model, the hold-out cross-validation method was employed, in which 70% dataset was used as training data and the remaining 30% was used as test data. The results show the prediction accuracy is high.

From these preliminary results, it can be concluded that the analyte gas can be represented by a feature vector containing multiple transient features. In combination with supervised machine learning, analyte gases can be discriminated and identified with excellent performance, such as high accuracy, sensitivity and specificity for NH_3 and PH_3 at ppb concentration level. This work may pave a path to design highly selective, highly sensitive, miniaturized, intelligent gas sensors for a wide spectrum of industrial gases.

REFERENCES

[1] H. Wu, Z. Ma, Z. Lin, H. Song, S. Yan, and Y. Shi, "High-Sensitive Ammonia Sensors Based on Tin Monoxide Nanoshells," Nanomaterials (Basel), vol. 9, no. 3, Mar 7, 2019.

[2] S. Ozdemir, and J. L. Gole, "A phosphine detection matrix using nanostructure modified porous silicon gas sensors," Sensors and Actuators B: Chemical, vol. 151, no. 1, pp. 274-280, 2010.

[3] "Preparation of thin gold-film electrode for an electrochemical gas sensor for phosphine and arsine," 1994.

[4] Y. S. Chung, K. Evans, and W. Glaunsinger, "Work function response of thin gold film surfaces to phosphine and arsine," Applied Surface Science, vol. 125, no. 1, pp. 65-72, 1998.

[5] R. Kumar, X. Liu, J. Zhang, and M. Kumar, "Room-Temperature Gas Sensors Under Photoactivation: From Metal Oxides to 2D Materials," Nano-Micro Letters, vol. 12, no. 1, 2020.

[6] S. Huang, A. Croy, L. A. Panes-Ruiz, V. Khavrus, V. Bezugly, B. Ibarlucea, and G. Cuniberti, "Machine Learning - Enabled Smart Gas Sensing Platform for Identification of Industrious Gases," Advanced Intelligent Systems, 2022.