Discrimination of Methanol from Ethanol Using Graphene-based Smart Gas Sensors

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Abstract— **Methanol and ethanol are physical-chemically similar volatile organic compounds and are widely used in the industry. Compared with ethanol, methanol is extremely toxic to human health by ingestion or inhalation. Therefore, it is of great importance to develop effective techniques to discriminate methanol from ethanol. The gold standard approaches for methanol and ethanol detection are gas chromatography-mass spectroscopy (GC-MS) and nuclear magnetic resonance (NMR), which are rather expensive and sophisticated. Alternatively, chemiresitive gas sensors show promising applications in volatile organic compounds detection. Here, we present the development of graphene-based smart gas sensors for methanol discrimination from ethanol. By using multiple transient-state features as the fingerprint information of gas, the selectivity of developed gas sensors is enhanced. This proposed strategy enables the graphene-based gas sensors with an excellent discrimination performance (accuracy-98.9%) leveraging supervised machine learning algorithms. This work paves the path to design a low-cost, low-power consumption, facile, highly sensitive, and highly selective smart gas sensor to discriminate methanol from ethanol, which could also be extended to other similar VOCs discrimination.**

Keywords—methanol and ethanol, gas discrimination, graphene, gas sensors, machine learning

I. Introduction

Methanol and ethanol are chemically similar volatile organic compounds (VOCs) and are widely used in various fields in the industry. For instance, methanol is commonly employed in dyeing, medicine, antifreeze industries, biodiesel fuels, petroleum industries, etc.; ethanol is widely used in food, pharmaceutical, and biological fields [1, 2]. Methanol and ethanol are also physically similar in odor and appearance. However, compared with ethanol, methanol is extremely toxic to human health by ingestion or inhalation, causing severe tissue damage to the human nervous and vision system, even death [3]. Thus, it is of the utmost importance to develop effective techniques to discriminate methanol from ethanol.

The traditional detection methods for methanol and ethanol include gas chromatography-mass spectroscopy (GC-MS) [4], nuclear magnetic resonance (NMR) [5], etc. These methods serve as gold-standard approaches for VOCs identification, while they suffer from disadvantages such as the requirement of expensive facilities and well-trained personnel, impeding their broad applications in our daily life. Recently, various sensors-based strategies, such as electrochemical [6], fluorescent [7], chemoresistive [8], etc., have been reported to detect VOCs. Among them, chemiresistive sensors show promising applications for VOCs detection due to their high sensitivity, simplicity, low fabrication cost, miniaturization potential, etc., which have attracted considerable attention in the academy and industry. Specifically, metal-oxide semiconducting (MOS) based gas sensors have demonstrated remarkably high sensitivity, whereas they suffer from poor selectivity for VOCs discrimination, particularly towards chemically similar compounds like methanol and ethanol [9, 10]. Moreover, MOS-based gas sensors generally require elevated working temperatures (e.g., 200–500 oC) to activate the adsorption of ionized oxygen species. Therefore, a facile, low-cost, low-power consumption, highly sensitive, and highly selective method for VOCs detection is in great demand.

Herein, we present a graphene-based smart gas sensor strategy to discriminate methanol from ethanol. Few-layer graphene flakes are deposited on interdigital electrodes (IDEs) acting as sensing element materials for developed chemiresistive gas sensors. Electrical resistance signal of the sensor device is acquired upon exposure to methanol or ethanol vapors following the same procedure at room temperature. Multiple transient features are extracted from the normalized response profile and employed as the distinctive fingerprint information of methanol and ethanol, improving the selectivity of developed gas sensors. Enhanced by supervised machine learning algorithms, the developed gas sensors demonstrate an excellent gas classification accuracy (98.9%) towards discriminating methanol from ethanol. Our work provides an efficient strategy to design low-cost, low-power consumption, facile, highly sensitive, and highly selective graphene-based gas sensors to discriminate methanol over ethanol, which could also be applicable for other similar gases discrimination.

II. Results and Discussions

The few-layer-graphene flakes were produced by electrochemical exfoliation of graphite (supplier: Sixonia Tech GmbH) and well dispersed in aqueous dispersion owing to the hydrophilic polymer functionalization on graphene flakes' surface [11, 12]. Afterward, graphene dispersion (3 mg/ml) was transferred onto the IDEs surface by dielectrophoresis (DEP, Vpp =10 V, f = 200 kHz) as sensing element materials on proposed chemiresistive gas sensors. The structure of IDEs features a gap size of 3 µm and a width size of 4 µm, respectively. More details on IDEs fabrication on silicon substrate can be referred to our previous published works [13, 14]. The resistance of fabricated graphene-based gas sensors ranges between 100 and 200 Ω. A bubbler evaporation system was designed to generate VOCs vapor as well as deliver vapors to the gas chamber by carrier gas, and the flow rate was controlled by the mass flow controller (MFC). Each cycle of gas sensing

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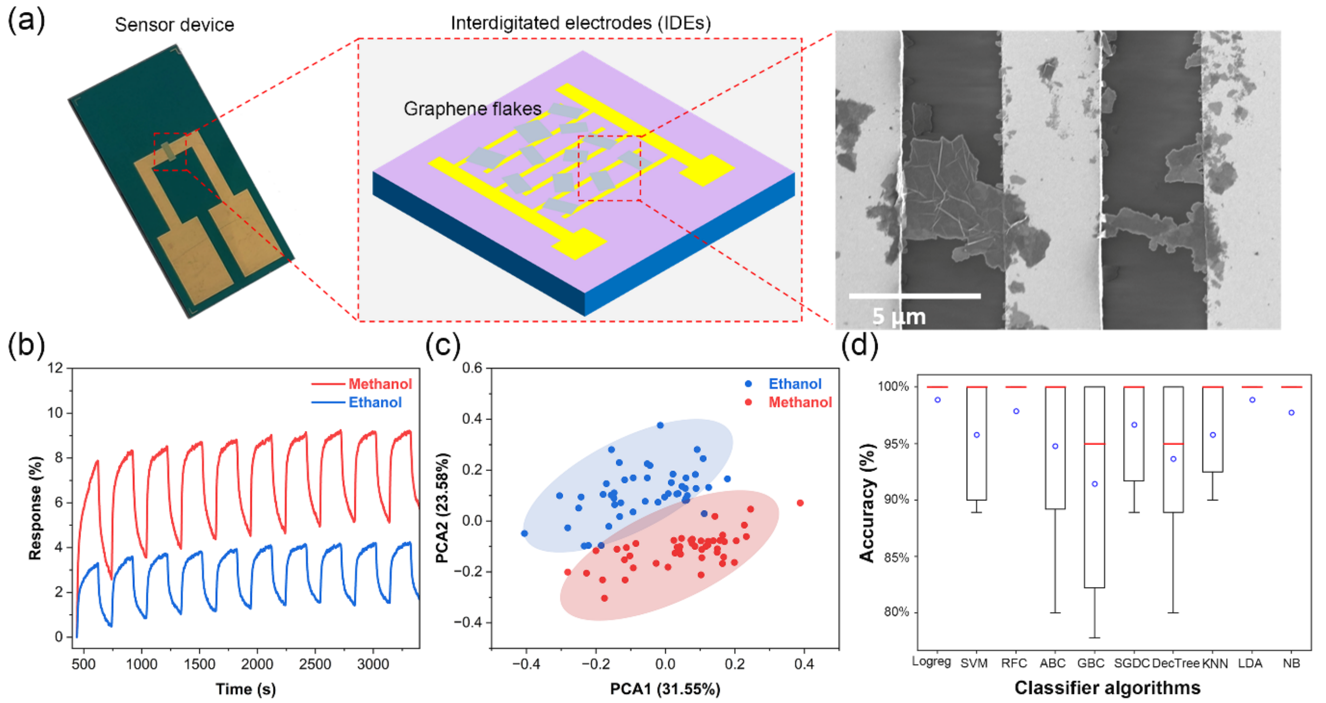

Figure 1. Graphene-based smart gas sensors to discriminate methanol from ethanol. (a) Interdigital electrodes sensor chip. (left) The optical image of sensor chip. (middle) The schematic image of interdigital electrodes structure. (right) SEM image of graphene flakes on surface of interdigital electrodes. (b) Gas sensing response profile of developed graphene-based gas sensors towards methanol and ethanol vapors. (c) The 2D principal component analysis (PCA) plot for analytes gas clustering. (d) The discrimination accuracy of methanol gas from ethanol gas with respect to a variety of classifier algorithms.

measurement contains two phases: the gas exposure phase (3 min) and the gas flushing phase (2 min). To collect much data for the VOCs discrimination performance evaluation by machine learning, 48 cycles of measurement were conducted for methanol and ethanol vapors. Instead of the use of a single steady-state feature (e.g., maximum response at steady state) from a single gas sensor, multiple transient-state features (number=15) were extracted from a single gas sensor, including exponential fitting parameters for response profile at gas exposure phase and gas flushing phase, distinctive parameters on the first derivative fitting profile and the second derivative fitting profile of gas response profile, transient-state response and the area under the response profile [15, 16]. These features were employed as the distinctive fingerprint information for each VOC to improve the selectivity of gas sensors.

The schematic of the designed IDEs structure is shown in Figure 1(a). The general lateral size of graphene flakes developed by electrochemical exfoliation of graphite is 0.5-2 µm. From the SEM image in Figure 1(a), several large graphene flakes aggregated together and contributed to an electrical conducting path between adjacent electrodes. The large lateral size of graphene flakes could reduce the number of graphene flakes required to bridge electrodes and minimize the contact resistance resulting from graphene interlayers. The gas sensing response signal of developed graphene-based gas sensors upon exposure to methanol vapor and ethanol vapor is illustrated in Figure 1(b), in which the sensing response toward methanol vapor is higher than methanol vapor under the same testing condition. This could be attributed to the distinctive interaction between methanol (or ethanol) vapors and functionalized graphene materials, such as binding energy, exchanged charge, etc., which can be further verified by density functional theory (DFT) simulation; on the other hand, it could be due to the concentration variance as the saturated vapor pressure of methanol vapor is higher than that of ethanol vapor on the same condition. To exclude the influence of concentration on the sensing response amplitude, the L2 normalization technique is utilized to normalize response data [15]. In total, 15 transient-state features are extracted from the normalized response profile to represent the fingerprint of each VOC. The principal component analysis (PCA) plot for these two gases is illustrated in Figure 1(c). As observed in the 2D PCA space, the methanol cluster could be separated from the ethanol cluster with few overlapping, indicating the high efficiency of employed multiple transient features. To demonstrate the identification performance using these transient features, the k-fold cross validation (k=10) is employed over a variety of common used classifier algorithms. The overall identification accuracy could reach more than 95% for most classifier algorithms. Remarkably, the identification accuracy between methanol and ethanol is up to 98.9% using the LDA classifier algorithm.

To conclude, we have presented an efficient strategy to discriminate methanol from ethanol using graphene-based gas sensors. The proposed graphene-based gas sensors exhibit response to both methanol and ethanol vapors. To improve the selectivity of graphene-based gas sensors, multiple transient-state features are acquired from the normalized response profile of both VOCs. With the k-fold cross-validation (k=10) approach, the developed graphene-based smart gas sensors exhibit excellent classification accuracy up to 98.9%. Our work paves the path to design a low-cost, low-power consumption, facile, highly sensitive, and highly selective graphene-based gas sensors for the discrimination of methanol over ethanol, which could also be extended to other similar gases discrimination.

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