Low-dimensional Nanomaterials-based Smart Gas Sensors for Odor Identification

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***Abstract*— Gas sensors play a crucial role in ensuring public safety, monitoring air quality, and detecting trace gases in industrial settings. The demand for gas sensors with high sensitivity, selectivity, efficiency, reliability, low cost, and low power consumption is substantial. Despite numerous proposals utilizing traditional metal oxide semiconductor materials, challenges persist in achieving satisfactory power consumption and selectivity. Herein, we address these challenges by developing smart gas sensors based on low-dimensional nanomaterials working at room temperature. Unlike their traditional counterparts, our sensors demonstrate improved selectivity and lower power efficiency. Combined with highly efficient machine learning algorithms, the low-dimensional nanomaterials-based gas sensors exhibit exceptional performance in both individual gas and complex odor identification. Our strategy paves the path to creating highly sensitive, selective, portable, and energy-efficient smart gas sensors using low-dimensional nanomaterials, catering to the growing needs of odor identification in various emerging fields.**

Keywords*— gas sensors, low dimensional nanomaterials, machine learning, complex odor, gas identification

I. Introduction

Generally, the critical component of the e-nose system is a sensor array consisting of multiple diverse sensors with semi-selectivity, which is analogous to the olfactory receptors in mammals and plays a paramount role in odor recognition. Based on the working principle, gas sensors encompass several types: optical, catalytic, surface acoustic wave, quartz crystal microbalance, electrochemical, chemiresistive types, etc. [1]. Among them, chemiresitive gas sensors have shown promising applications in various fields due to their simple electrical characteristics and readout interface circuit[2]. Regarding the sensing element material, gas sensors could be classified into the following categories: metal-oxide-semiconductor (MOS), conducting polymers, zero-dimensional nanomaterials, one-dimensional nanomaterials, and two-dimensional nanomaterials types, etc. MOS-type gas sensors have been widely configured in commercial e-nose products since the 1970s because of their low cost, feasible fabrication, sound sensitivity, [3] etc. Nevertheless, MOS-type gas sensors might not fit well for miniaturization and energy-efficient trends of e-nose due to their high operating temperatures (300–500 °C) [4]. In contrast, the main problems of conducting polymer-type gas sensors are low sensitivity at room temperatures, low surface area, modest stability, and relatively low conductivity[5]. Consequently, currently commercialized e-nose products are usually large, expensive, non-portable, and laboratory instruments. Therefore, new-generation gas-sensing element materials and efficient recognition algorithms are in great demand in the e-nose system.

In the past decades, with the successful discoveries of many low dimensional (low-d) nanomaterials, considerable effort has been made to investigate these nanomaterials as sensing materials in chemiresistive type gas sensors. Single-walled carbon nanotubes (SWCNTs) are quasi-one-dimensional nanomaterials exhibiting extremely high surface-to-volume and length-to-diameter ratios [6]. In 2000, the single-walled carbon nanotubes (SWCNT) based gas sensor was first demonstrated for gas detection (NO_2 and NH_3), and their work laid the foundation of SWCNT in the gas sensing applications[7]. Graphene, an allotrope of SWCNT, which is a two-dimensional (2D) material with a single layer of atom thickness formed in a honeycomb crystal lattice structure, has attracted enormous attention in numerous fields owing to the exceptional electrical, mechanical, and thermal properties[8]. In particular, graphene possesses remarkably high electron mobilities and ultra-high surface-to-volume ratio, stimulating considerable interest in highly sensitive gas sensing applications since 2007[9]. Graphene has demonstrated outstanding performance in gas sensing applications compared to traditional MOS-type sensing materials, such as high sensitivity, excellent reversibility, selectively tunable, and low operation temperature (usually room temperature). MXenes, a class of 2D inorganic compounds, comprises atomic layers thickness of transition metal carbides, nitrides, or carbonitrides. MXenes exhibit metallic conductivity, abundant surface-terminated functionality, hydrophilicity for water-based processing, and extraordinary electrical and electrochemical properties [10], which have become emerging sensing materials for gas sensors since 2017 [11]. Metal-organic frameworks (MOFs), a group of compounds consisting of metal clusters coordinated to organic ligands, have recently gained considerable attention in the field of gas sensing due to their porosity (aperture size and geometry), modularity, crystallinity, and tailor-made responsiveness to external stimuli [12], etc. Compared with traditional MOS-type materials-based gas sensors, these low-d nanomaterials-based gas sensors exhibit high performance with lower power consumption (mostly at room temperature), demonstrating a promising future in both traditional and emerging applications.

Currently, in the pattern recognition system of the state-of-the-art e-noses, a single thermodynamic feature extracted from each sensor (e.g., steady-state response or maximum response) is prevalently used [13]. Nevertheless, transient-state kinetical features extracted from sensing response profiles are usually undervalued, which are inherent to the adsorption dynamic or desorption dynamic interaction between sensing element materials and gas molecules [14].

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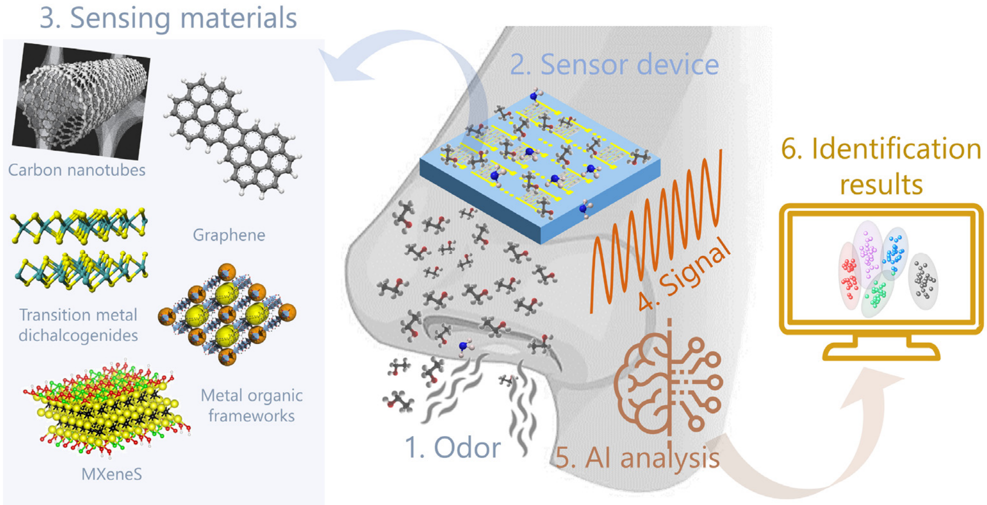

Figure 1. Scheme of low-d nanomaterials-based smart gas sensors for odor identification.

Moreover, in terms of the pattern recognition system, transient features-based e-noses exhibit many benefits over the conventional single thermodynamic feature-based e-nose, such as enhanced selectivity, shorter acquisition time, prolonged sensor lifetime, etc.

Herein, we present the development of low-d nanomaterials-based smart gas sensors working at room temperature and their application for odor discrimination and identification. Low-d nanomaterials are employed as sensing element materials in our chemiresistive type gas sensors. The sensor system configuration varies from the particular scenario, such as single-channel gas sensors, multiple-channel gas sensors, etc. Multiple transient features are extracted from the sensing response profile of each gas and represent the smellprint of each gas. Combined with highly efficient machine learning algorithms, the proposed low-d nanomaterials-based gas sensors exhibit excellent performance for individual and complex odor identification. Our strategy paves the path to develop highly sensitive, selective, portable and energy-efficient smart gas sensors for odor identification in various emerging fields.

II. Results and Discussions

The schematic of our proposed smart gas sensors is shown in Figure 1. The typical workflow of the low-d nanomaterials-based smart gas sensors is as below: odorant gas molecules reach the sensor surface and interact with low-d nanomaterials deposited on the gas sensor device, varying the concentration of carriers (holes or electrons) in low-d nanomaterials. The adsorption or desorption event could be characterized by the electrical resistance signal of sensor device itself. The sensing response profile toward each odor is acquired, and transient-state features are extracted from the sensing response profile, which is utilized as the smellprint of the odorant. Combined with an efficient artificial intelligence algorithm, the proposed smart gas sensors present classification and prediction results for individual gas or complex odor.

In Figure 2(a), the identification results of APTS functionalized smart gas sensors towards the detection of various odorant molecules is presented. The developed APTS functionalized smart gas sensor consists of a single channel gas sensor instead of a sensor array in a conventional e-nose system and works at room temperature. Instead of traditional steady-state features (maximum steady-state response, etc.), kinetically transient-state features were extracted from the gas sensing response profile, which makes the best use of the characteristic response profile of odor sensing. Noncovalently functionalized graphene was applied as sensing element materials and enabled the devices with merits of selective adsorption and ultrahigh sensitivity. Incorporating with supervised machine learning classifier algorithm (e.g., LDA), the gas sensors demonstrate ultrahigh odor identification accuracy (97.5%) towards the detection of various individual odors. Moreover, the identification results of CuPc functionalized smart gas sensors towards the detection of industrial gases (e.g., NH_3, PH_3) are depicted in Figure 2(b). Graphene is exfoliated and successfully functionalized by copper phthalocyanine derivate (CuPc). Multiple transient features are employed as the smellprint of these two gases. In combination with efficient machine learning techniques (such as LDA), the developed CuPc functionalized graphene nanosensor demonstrates an excellent gas identification performance at low concentration (1000 ppb).

Meanwhile, the identification results of Au nanoparticles functionalized graphene for the detection of complex odor is illustrated in Figure 2(c) and (d). Here we take the vapor of three types of brewed coffee as an example. It has been well known that coffee aroma is complex compound containing more than 100 types of volatile organic compounds (VOCs) that exhibit various qualities, various levels of intensity, and various concentrations. The gold standard technique for complex odor analysis is gas chromatography-mass spectrometry (GC-MS), which requires expensive instruments and well-trained personnel. From the classification results and confusion matrix results, it indicates that the developed Au nanoparticles functionalized graphene smart gas sensors demonstrate excellent performance.

To sum up, this work represents a strategy to develop highly sensitive, highly selective, and low-cost smart gas sensors for detecting and identifying individual gas (e.g., NH_3, PH_3, VOCs odor, etc.) and complex odor at room temperature. Low dimensional nanomaterials exhibit a variety of benefits over traditional MOS materials as sensing element materials, such as surface-terminated functionality, tunable selectively, low operation temperature, etc. The proposed strategy may allow for gas discrimination and odor

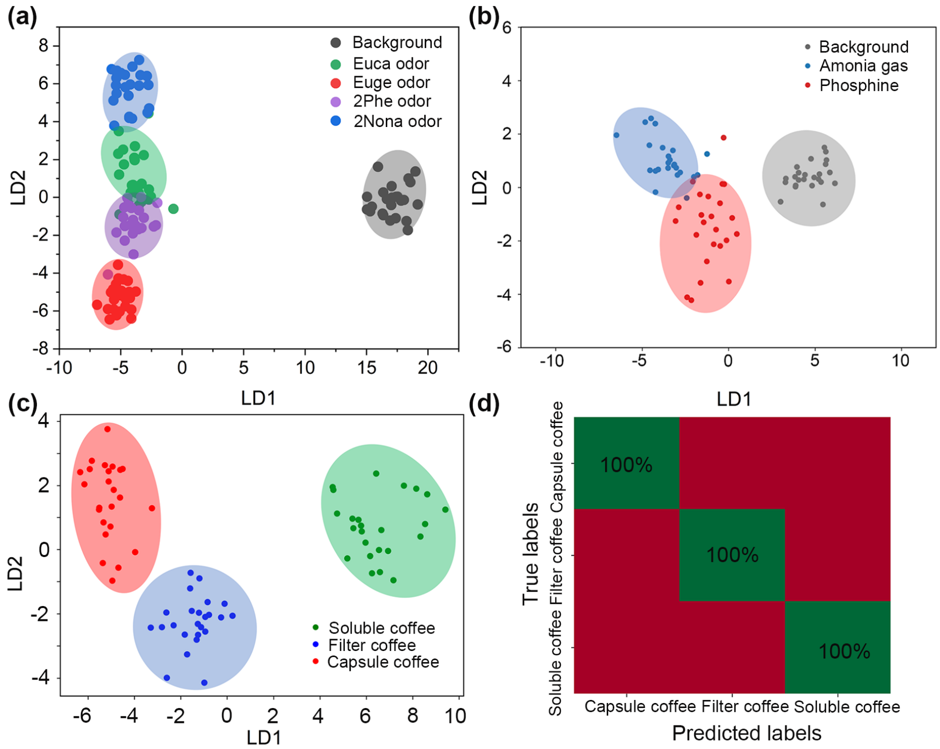

Figure 2. Identification results of graphene-based smart gas sensors towards the detection of individual gas and complex odor. (a) The identification result of APTS functionalized graphene-based smart gas sensors towards the detection of individual odorants: Eucalyptol (Euca), Eugenol (Euge), 2-nonanone(2Nona), 2-phenylethanol(2Phe). (b) The identification result of CuPc functionalized graphene-based smart gas sensors towards the detection of industrial gases: NH_3 and PH_3 at 1000 ppb concentration. (c) The identification result of Au nanoparticles-functionalized graphene-based smart gas sensors towards the detection of the vapor of three types of brewed coffee: soluble coffee, filter coffee, and capsule coffee. (d) The confusion matrix result of coffee identification, indicating an identification accuracy of 100%.

identification of a broad spectrum of odor molecules in various domains, such as smart farming, environmental monitoring, public security, disease diagnosis, etc.

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