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Recent advances in graphene based gas sensors

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ABSTRACT

Graphene, a single, one-atom-thick sheet of carbon atoms arranged in a honeycomb lattice and the two-dimensional building block for carbon materials, has attracted great interest for a wide range of applications. Due to its superior properties such as thermo-electric conduction, surface area and mechanical strength, graphene materials have inspired huge interest in sensing of various chemical species. In this timely review, we discuss the recent advancement in the field of graphene based gas sensors with emphasis on the use of modified graphene materials. Further, insights of theoretical and experimental aspects associated with such systems are also discussed with significance on the sensitivity and selectivity of graphene towards various gas molecules. The first section introduces graphene, its synthesis methods and its physico-chemical properties. The second part focuses on the theoretical approaches that discuss the structural improvisations of graphene for its effective use as gas sensing materials. The third section discusses the applications of pristine and modified graphene materials in gas sensing applications. Various graphene modification methods are discussed including using dopants and defects, decoration with metal/metal oxide nanoparticles, and functionalization with polymers. Finally, a discussion on the future challenges and perspectives of this enticing field of graphene sensors for gas detection is provided.

1. Introduction

Gas sensors play a significant role in numerous application fields such as environmental monitoring, industrial production and safety, medical diagnosis, military and aerospace [1]. Even though solid state gas sensors possess advantages such as small size, low power, high sensitivity and low cost for detecting very low concentrations of a wide range of gases in the range of parts-per-million (ppm), they suffer from problems associated with long term stability and limited measurement accuracy [2]. Nanotechnology provides numerous opportunities to develop the next generation gas detectors with enhanced sensor performance such as ultrahigh sensitivity at extremely low concentrations, high specificity, fast response and recovery, low power consumption, room temperature operation and good reversibility by employing novel nanostructures as sensing elements [3,4].

The most important parameter that determines the sensitivity of gas sensors is their specific surface-to-volume ratio, which is much higher in nanostructure based sensors than conventional microsensors. The higher detection area of the nanostructured materials leads to greater adsorption of gas species on them and thus increased sensing capability. Hence they are promising candidates as sensing elements for developing highly efficient gas sensors [5]. So far, several nanostructured systems have been successfully employed as sensing materials that include one dimensional nanowires (1-D NWs) [6] to two dimensional carbon nanotubes (2-D CNTs) [7]. Detection limit of as low as few tens of parts-per-billion (ppb) has been achieved using such systems [8]. In addition to increased sensitivity, the use of nanostructure-based devices for chemical detection has also shown other benefits such as low power consumption, lightweight and miniaturized integration.

Amongst nanostructured gas sensing systems, nano-carbon based materials proved to be promising due to their intrinsic electrical properties which are highly sensitive to the changes in the chemical environments [9–12]. Further, the high surface area, high chemical and thermal stability and functionalization capability of carbon based nanostructures make them suitable for high performance label free chemical sensing [13].

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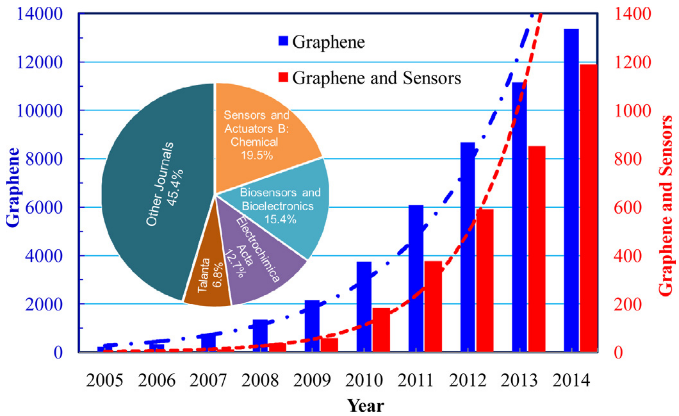

Fig. 1. Number of annual publications on "graphene" and "graphene and sensors" according to Scopus Database. The dashed lines are exponential fitting of the number of publications. Inset: where "graphene and sensors" publications have appeared.

Recently, graphene, a carbon allotrope has attracted a great deal of interest due its extraordinary electronic, chemical, mechanical, thermal and optical properties which bestowed graphene as the miracle material of the 21st century [14]. Graphene based materials have already demonstrated their applicability in fields like energy storage, biomedical, electronics, etc. [15]. Graphene materials are used as sensing materials due to its high specific surface area and unique electrical properties such as high mobility and low electrical noise. Wide range of chemicals, biomolecules and gas/vapors has been detected using graphene based sensors [16–20]. However, so far, only few articles review this exciting field of gas sensing using graphene materials [16,19,20]. Only a handful of review articles dedicated to graphene based gas sensing have been published during the last few years covering diverse aspects of graphene for gas sensing, but none of these reviews discusses the effect of modifications and the theoretical implications. The interest in graphene for sensing applications is continuously increasing as evident by the exponential growth in number of publications dedicated to graphene-based sensors (Fig. 1). Based on Scopus search using "graphene" and "graphene and sensors" as keywords, the publications on "graphene and sensors" represent about 7% of the "graphene" publications with more than half of these "graphene and sensors" publications appears in Sensors and Actuators B: Chemical (20%), Biosensors and Bioelectronics (15%), Electrochimica Acta (13%) and Talanta (7%), as shown in the inset of Fig. 1.

This review presents a critical summary of the state of the art of the research on graphene and modified graphene based gas sensors. The effects of modifying graphene and its derivatives with dopants, defects, metal/metal oxide nanoparticles and polymers on the sensitivity and selectivity towards various gases are discussed in detail. Although the majority of the reviewed publications are experimental, we also discuss the published theoretical quantum mechanical calculations and simulation studies on the adsorption of gas molecules on pristine and modified graphene. Before discussing the very recent research that focuses on the modifications of graphene and its derivatives to improve sensing performance, initial studies on gas sensors with pristine graphene (PG), graphene oxide (GO) and reduced graphene oxide (RGO) are also covered. Finally, a critical analysis of the present status and future developments of graphene based sensing devices is provided.

2. Graphene: Synthesis and properties

Structurally, graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice with carbon–carbon bond length of 1.42 Å. A stack of large number of graphene sheets with 3.35 Å interplanar spacing forms graphite; 1-mm thick graphite flake contains ~3 million layers of stacked graphene sheets. Graphene can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. Graphene sheets composed of few atomic layers such as few layer graphene (FLG) exhibits semi metallic electronic properties with zero energy bandgap [21].

Geim and co-workers [21] at the University of Manchester reported the isolation of graphene sheets by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG); this method is commonly known as the scotch-tape method. Since then, graphene has become the topic of extensive research for scientists around the globe due to its fascinating structural, electrical, optical and mechanical properties. The production of graphene and the implementation of graphene-based devices for various applications had shown great progress since 2004.

Graphene can be synthesized by various methods such as exfoliation–intercalation–expansion of graphite [22], arc-discharge techniques [23], epitaxial growth on silicon carbide (SiC) [24], unzipping CNTs [25]. Chemical vapor deposition (CVD) growth [26,27] is another technique capable of mass producing large areas of single layer graphene (SLG) sheets. CVD growth provides large detection area, makes sensor device fabrication easier and hence suitable for sensing applications [15]. The thermal [28] or chemical reduction of graphite oxide [29], is the most commonly employed way to synthesize graphene due to higher cost-effectiveness. Even though various techniques have been developed for graphene synthesis, high yield, economical production is still not widely available and this slow the commercialization of many practical graphene applications.

This interesting material has shown great potential for various applications such as solar cells [30], energy storage [31], fuel cells [32], biotechnologies [33], electronics and photonics [34] owing to its combination of extraordinary properties such as high carrier mobility (~2,00,000 $cm^2/V\,s$ at room temperature (RT)) [35], high carrier density (10^{13} cm^{-2}) [21], excellent electrical (5600 S/m) and thermal (~3000 W/mK) [36] conductivity and exceptionally high strength (1.2 GPa) and modulus (1.05 TPa) [37,38]. In addition to these fascinating properties, graphene has also been demonstrated as a promising sensing element [39] that can find applications in various areas due to its large surface area (2630 m^2/g) [40] and high signal-to-noise ratio arising from low intrinsic noise. Graphene also exhibits many intriguing properties such as anomalous quantum Hall effect at RT [41], ambipolar electric field effect [21], high elasticity [38] and detection of single molecule adsorption events [39] useful for chemical sensing.

3. Graphene for gas sensing

Based on its structural features, graphene materials (PG, GO and RGO) have presented a distinct gas sensing capability. The two dimensional structure of graphene makes the electron transport through graphene highly sensitive to the adsorption of gas molecules [42]. The adsorption of gas molecules on graphene's surface leads to changes in its electrical conductivity that can be attributed to the change in the local carrier concentration induced by the surface adsorbates which act as electron donors or acceptors [39]. All these materials have different electrical conductivity and surface functional groups, which play an important role in the gas sensing mechanism. For example, since PG possesses low intrinsic noise and high electrical conductivity even in absence of charge carriers, few charge carriers induced by the gas adsorbates lead to notable changes in charge carrier density resulting in detectable