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A Review on Graphene- Polymer Combined Quaternary Nanocomposite Based Gas Sensors with Potential Applications

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Abstract: Gas sensors can detect combustible, explosive and toxic gases, and have been widely used in safety monitoring and process control in residential buildings, industries and mines. Recently, graphene-based hybrids were widely investigated as chemiresistive gas sensors with high sensitivity and selectivity. This systematic review is therefore timely and necessary to evaluate the success of graphene-based hybrids on gas detection and to identify their challenges. We review the sensing principles and the synthesis process of the graphene-based hybrids with noble metals, metal oxides and conducting polymers to achieve better understanding and design of novel gas sensors. Our review will assist researchers to understand the evolution and the challenges of graphene-based hybrids, and create interest in development of gas-sensing techniques. In this paper, the main characteristics of gas sensor are firstly introduced, followed by the preparation methods and properties of graphene. In addition, the development process and the state of graphene gas sensors are introduced emphatically in terms of structure and performance of the sensor. The emergence of new candidates including graphene, polymer and metal/metal oxide composite enhances the performance of gas detection significantly. Finally, the clear direction of graphene gas sensors for the future is provided according to the latest research results and trends. It provides direction and ideas for future research.

Keywords: Graphene, Chemiresistive gas sensor, Gas detection, Graphene-based hybrid, Graphene-metal hybrid, Graphene-metal-oxide hybrid, Graphene-polymer hybrid, Nanocomposite, Sensing

Introduction

With the improvement of industry, living standards and the emphasis on the environment, the detection of toxic and hazardous gases is facing higher challenges. In addition, sensors sensing the surrounding gas environment play an important role in this field. Gas sensors are devices that convert the gas volume fraction into corresponding electrical signal [1]. They are of crucial importance in environmental monitoring, industrial chemical processing, public safety, agriculture and medicine [2]. With the development of science and technology, the development of gas sensors towards high sensitivity, high selectivity, fast response, low cost, low power consumption, stability and portability has led to the search for new and superior gas-sensing materials [3]. Metal oxide semiconductor (MOS) gas sensors are the most wildly used gas sensors in the world for production and use due to its high sensitivity and fast response time [4]. The sensing mechanism of the MOS gas sensors is attributed to changes of electric charge carriers caused by oxidation or reduction reactions occurring at the surface of the metal oxide [5]. However, they still have the disadvantages of short life, poor selectivity and high operating temperature. Sensitivity is not sufficient for the application of precision measurement. The key indicator of material gas sensitivity is the specific surface area, which is the total surface area of a material per unit of mass [6]. The large specific surface area of nanomaterials facilitates the adsorption of gas molecules, thereby enhancing the sensitivity of gas detection. Theoretical and experimental results showed that [7] graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), exhibit large specific surface area, excellent conductivity, and easy adsorption of gas molecules, and the surface can easily be modified by functional groups, so it has good gas sensing properties. Graphene, a monolayer of graphite sheet consisting of sp2 hybridized carbon atoms covalently bonded to three other atoms which was first isolated by Geim and Novoselov using micro-mechanical peeling of graphite in 2004, so they won the 2010 Nobel Prize in Physics [8]. Graphene is the thinnest and highest strength material in nature at present and has the advantages of strong electric conductivity and heat conductivity, and is almost transparent and dense, thus attracts people's attention [9]. Nowadays, there are many studies about graphene gas sensors focused on the performance improvement in the field of composite materials, computational chemistry and Micro-Electro-Mechanical System (MEMS). Considering the practical application of graphene gas sensor, we need to find the most potential direction. In this article, the development process and the state of art of graphene gas sensors are introduced. The direction of graphene gas sensors for the future is also provided. The review provides important reference for follow-up research work. Besides the surface modification by physical methods, chemical modification has commonly been used to enhance the sensing properties of graphene [10]. In particular, graphene-based hybrids consisting of graphene and traditional gas-sensing materials (e.g., noble metals, metal oxides or conducting polymers) display not only the individual properties of the traditional gas-sensing materials and graphene, but also additional novel properties due to the synergistic effect between them. The outstanding gas-sensing properties of graphene greatly depend on the number of layers and its dispersion. Due to van der Waals and ð-ð stacking interactions among individual graphene sheets, they have a tendency to aggregate when graphene-dispersion solutions are dried. Incorporation of nanostructures of traditional gas-sensing materials into graphene sheets prevents graphene from becoming agglomerated and also helps to achieve a good distribution of nanostructures. Thus, the effective surface area available for the gas interaction increases by several times. These nanostructure-graphene hybrids are prepared by an *in-situ* method, where nanostructures are prepared in the presence of graphene solution, or by directly mixing two previously prepared solutions.

Although some reviews about graphene-based gas sensors were published recently [11–14], little attention was given to hybridized graphene gas sensors. However, increasing effort has been devoted to development of the hybridized graphene gas sensors. A systematic review is therefore timely and necessary to evaluate the success and to identify the challenges for graphene hybrids in gas detection. Here, we review the sensing mechanism and unique performance of the graphene-based hybrids as gas sensors. This review will help researchers understand the evolution and the challenges of graphene-based hybrids, and also further stimulate interest in the development of gas-sensing techniques.

We introduce hybridized graphene gas sensors by dividing them into four types according to their sensing principles, i.e., the hybrids of graphene with noble metals, metal oxides and conducting polymers, respectively, and their ternary hybrids.

2. Experimental

2.1 Synthesis of Graphene & Graphene based material

There are mainly four approaches to synthesize single layered or few-layered graphene: micromechanical exfoliation, epitaxial growth, vapor deposition, and chemical reduction [15–18]. Novoselov et al. used scotch tapes to repeatedly peel flakes of graphite off the mesas which were fixed onto a SiO2/Si substrate, and the high-purity, single layered graphene was obtained [19]. By micromechanical exfoliation of highly ordered pyrolytic graphite, crystalline graphene nanosheet with large surface areas and a small number of layers could be obtained [20]. This method is very simple and does not need any special facilities. However, it is limited to laboratory research because of the small size and inefficiency of the production. Berger and his co-workers got graphene thin films which exhibited remarkable two-dimensional (2D) electron gas behaviors through thermal decomposition on the (0001) surface of 6H-SiC [21]. Epitaxial growth, compared with mechanical exfoliation, can realize the preparation of graphene with larger sizes and higher qualities. Hence, this approach is of significant importance for graphene semiconductor devices. Although a great breakthrough has been made for this technique, there is still a long way to go toward mass production of the graphene with uniform thickness and acceptable cost. Chemical vapor deposition (CVD) is the most extensively used method in industrial manufacture considering the merits of controllable sizes and structures. By pyrolysis of carbon-containing compounds, graphene was grown on the surfaces of transition metals, such as Cu, Pt, Ni, Ru, and Ir [22]. Copper foil is the most common substrate material to build single-layered graphene. Li and his group have successfully synthesized large-area and uniform graphene films on copper foils with a high quality by CVD techniques using methane as carbon source [23]. In 2006, Stankovich et al. created a bottom-up approach when they incorporated graphene sheets in a composite material and the far-reaching method, which called chemical reduction of graphene oxide, pave the way for graphene's large-scale production, modification, and application [24]. Figure 6 displays the fabrication process flow of graphene–polymer composite. In 2009, Tung et al. reported a versatile solution-based process for the largescale production of single-layered chemically converted graphene over the entire area of a silicon/SiO2 wafer [25]. Brodie method, Staudenmaier method and Hummers method are three main ways to form GO. Hummers method is becoming the most popular approach to synthesize GO by virtue of its merits, including rapid, easy and relatively safe properties. Various modified Hummers methods have been reported to promote the progress of GO preparation [26].

3. Result & Discussion

3.1 Graphene Gas Sensor

3.1.1 Gas Sensors Based on Pristine Graphene

In 2007, Schedin et al. used mechanically stripped graphene for the detection of individual gas molecules [27]. In the experiment, the response of graphene to 1 ppm ammonia (NH3), carbon monoxide (CO), nitric oxide (NO) and water vapor was measured and the change of resistance was recorded. Figure 2 shows that the resistance of graphene increases after access NH3 and CO. The electron transferred to the graphene material as these two gas molecules adsorbed on the surface of graphene, resulting in reduced conductivity, which increased resistance. The opposite happened after access to water vapor and nitrogen dioxide (NO2).

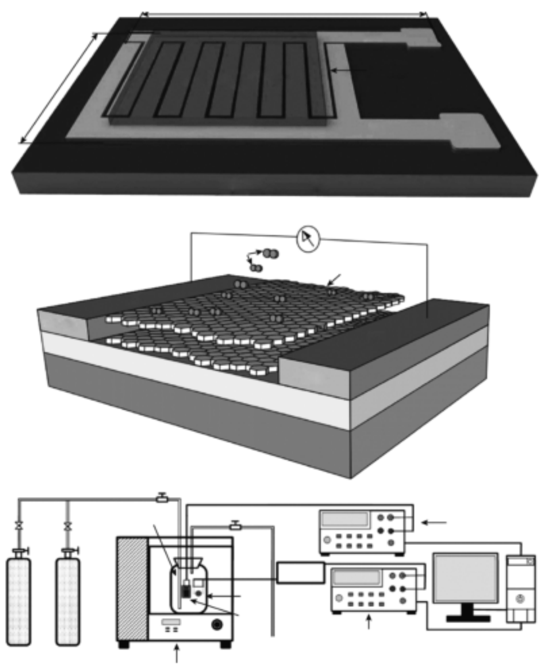

Figure 1. Typical schematic diagram of a chemiresistor, b FET, and c testing system of gas sensors with chemiresistor structure. Adapted from reference [58, 59]

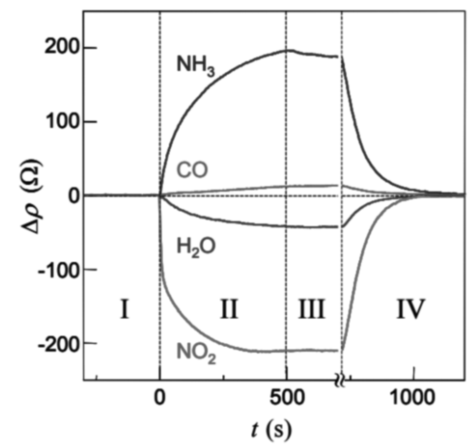

Figure 2. Chemical sensitivity of grapheme [28].

In 2012, Hwang et al. from Yonsei University studied the response of graphene to NH3 with different layer number and length-to-width (L/w) ratio [28]. The graphene was prepared from highly oriented pyrolytic graphite (HOPG) through mechanical cleavage. Figure 3a shows the different layers of graphene have similar responses to NH3, indicating that the graphene layer (mono-, bi- and tri-layer) has no obvious influence on the sensitivity of gas sensing. Figure 3b indicates that the response time and response intensity obviously changes with the change of L/w. To sum up, the key factor that affects the sensing of NH3 by graphene is the aspect ratio rather than the layers.

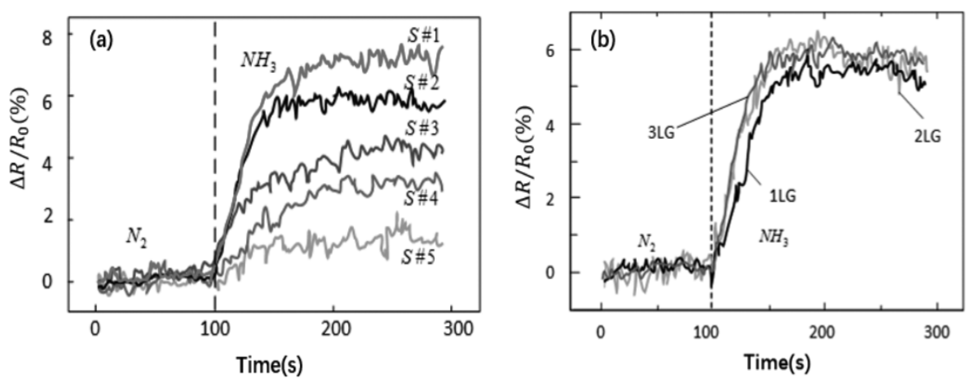

Figure 3. (**a**) Comparison of the response of monolayer, double and triple layer graphene to NH3 with a flow rate of 200 mL/min; and (**b**) The change in response due to L/w ratio and surface area of graphene with NH3 flowing at 200 mL/min [29].

In 2017, Ricciardella F from Delft University of Technology prepared the graphene sensing layer by chemical vapor deposition on pre-patterned catalyst and then it was eased onto the underlying SiO2 through a completely transfer-free process [29]. The gas sensing materials had different line width: 5 and 10 _m. The latter one, having a sensing area reduced by half with respect to the former one, showed a higher sensitivity upon exposure towards both gases, indicating that the sensitivity can be modulated by varying the geometry of the device exposure area. Yanyan Wang et al. from Jiangsu University proposed a vertical responsive gas sensor based on three-dimensional porous graphene ultrathin film, as shown in Figure 4 [30]. Different from the flat transportation response, the current in the structure flowed in a direction perpendicular to the graphene film, which avoided the impediment to carriers due to the graphene's adhesion to gas molecules in the plane.

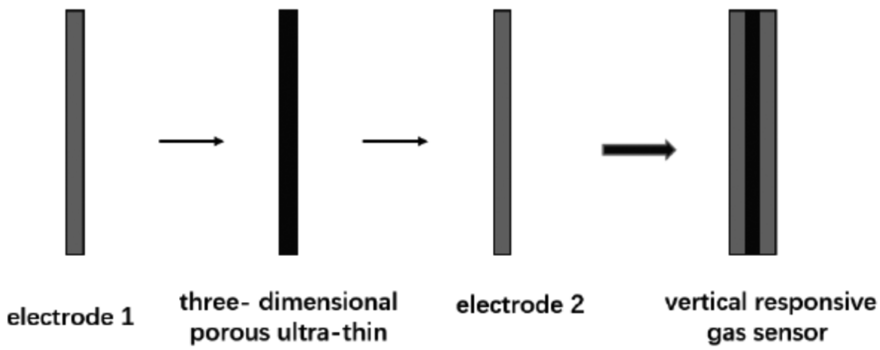

Figure 4. Vertical responsive gas sensor based on 3D porous graphene ultrathin film [30].

In 2017, Wei Wei et al. from Key Laboratory of Optoelectronic Technology & Systems, Chongqing University proposed a graphene-based long-period fiber grating surface plasmon resonance (LPFG SPR) sensor for high-sensitivity gas sensing and its preparation process, as shown in Figure 5 [31]. A monolayer of graphene was coated onto the Ag film surface of the LPFG-SPR sensor, which increased the intensity of the evanescent field on the surface of the fiber, thereby enhancing the interaction between the SPR wave and molecules. Such features significantly improved the sensitivity of the sensor. The experimental results demonstrated that the sensitivity of the graphene.

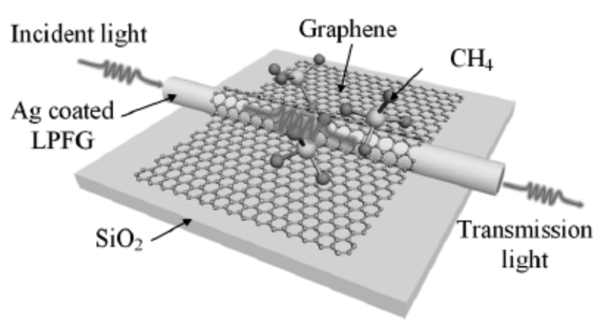

Figure 5. Schematic of the graphene-based LPFG SPR sensor [31].

3.1.2 Gas sensor of graphene with metal oxides

Metal oxides (e.g., SnO2, ZnO, In2O3 and Co3O4) have been widely used as gas sensors because of their advantages of low cost, easy production, compact size and simple measuring electronics [31–33]. However, the morphology and the structure of the sensing materials significantly influence their sensing performance, so various nanostructured metal oxides have been prepared to improve gas-sensing properties [32–35].

As a recent research interest, the hybrids of graphene with metal oxides were extensively investigated as gas-sensing materials to improve sensing performance. The synergistic effect between graphene and metal oxides can be summarized as follows:

- graphene can control the size and the morphology of metal oxides during synthesis;
- graphene increases the conductivity of metal oxides, which may rapidly transfer the electrons acquired from the surface reaction of gas molecules and metal oxides to electrodes;
- there are p-n junctions between p-type graphene and n-type metal oxides, which may modulate the space-charged layers at the interfaces between graphene and metal oxides; and,
- metal-oxide nanostructures can prevent aggregation of graphene.

3.1.3 Gas sensor of graphene with conducting polymers

In the past few decades, conducting conjugated polymers, such as polythiophene (PTh), polyaniline (PANI), and polypyrrole (PPy), which have ð-conjugated carbon chains, have been investigated intensely, especially for their gas-sensing properties. They have exhibited many excellent properties, such as electrochemical reversibility, environmental stability, high conductivity, good mechanical performance and ease of preparation through chemical and electrochemical methods. Moreover, they possess advantages over metal-oxide gas sensors due to their capability to operate at room temperature [36] and excellent mechanical characteristics for fabricating flexible gas sensors [37,38].

Recently, graphene was used to hybridize with them to enhance their gas-sensing performance further [39–42]. Table 3 compares the gas-sensing performance of conducting polymer/graphene hybrids, and it shows that they all operated at room temperature because most of the conducting polymers also operated at room temperature. The synergistic effect enhances the gas-sensing performance of hybrids.

Graphene can tune the morphology and enhance the electrical conductivity of the conducting polymer, which may enrich functional groups for gas-molecule adsorption compared to a pure graphene sensor. The electrical conductivity of hybrids is usually adjusted by controlling the weight percentage of graphene [43].

During the typical sensing process, the analytes directly adsorb on the surface of conducting polymers and then react with them. The electron charges move from the analytes to the conducting polymers and then transfer to the graphene.

The synergistic effects on gas sensing were investigated by Jang et al. [44], who compared the sensing properties of the hybrids of PPy with different graphitic materials, including GO and RGO. The PPy/GO hybrid showed lower sensitivity than the PPy/RGO hybrid because the electron-charge transfer between PPy and GO was difficult, particularly due to the poor interfacial affinity and the lower electrical conductivity of GO. The electron charge acquired from the analyte on the surface of PPy could not be transferred effectively to the electrode via GO. The PPy/RGO hybrid overcame the drawback by using the more conductive RGO, and showed higher sensitivity because of improved electrical conductivity. Besides, RGO played an important role in tuning the morphology of the hybrids. PPy/RGO hybrids showed less aggregation among those hybrids, when PPy was uniformly and thinly coated on RGO.

Since conducting polymers are usually dense film structures, it is difficult for gases to diffuse into the inner region, so, for high sensitivity, it is critical to tune the morphology of the hybrids. To obtain a uniform thin film, Gross et al. [45] synthesized the hybrid of poly (diallyldimethyl ammonium chloride) (PDAC) and RGO by the layer-by layer technique, which could discriminate between VOCs, including toluene, gasoline, ethanol, chloroform, and acetone. Tung et al. [46] prepared a thin hybrid film of poly(3,4-ethylenedioxythiophene) (PEDOT) and RGO using vapor-phase polymerization. Compared to traditional chemical polymerization, vapor-phase polymerization was a rapid, simple method to fabricate high-quality CP/RGO thin film. Yang et al. [47, 48] synthesized porous PEDOT on single layer RGO using a fast baking treatment to improve the capability of gas diffusion. The porous PEDOT/RGO hybrid exhibited response two orders higher than the bare RGO and the common RGO/PEDOT hybrid, and response and recovery faster than that of the bare RGO, due to the porous structure of PEDOT.

Huang et al. [49] fabricated another hybrid, in which PANI-NPs were anchored on the surface of RGO sheets by using RGO/MnO2 hybrids as both templates and oxidants for aniline monomer during polymerization. The RGO/PANI hybrid exhibited much better response to NH3 gas than those of the bare PANI nanofiber and bare graphene because of the synergetic behavior between the RGO sheets and the PANI-NPs. The PANI-NPs, instead of PANI film, were coated onto the RGO, enlarged the surface area and enhanced the ability of gas diffusion.

Another sensing mechanism for conducting polymer/graphene hybrids was proposed by Konwer et al. [50], who prepared a polyaniline/GO (PANI/GO) hybrid and investigated its sensing properties to methanol. It was proposed that the change in conductivity of the hybrid was caused by the strong hydrogen bonding between methanol and PANI, which disrupted the extended H-bonding between GO and PANI. After the removal of methanol, possible reformation of the extended H-bonding between GO and PANI took place and the conductivity returned to its original value.

In 2014, Huiling Tai et al. from University of Electronic Science and Technology of China proposed a graphene-based ternary composite film gas sensor and a preparation method thereof [51], as shown in Figure 6. The gas-sensitive material is a composite of graphene, metal or metal oxide nanoparticles and conductive polymer compound.

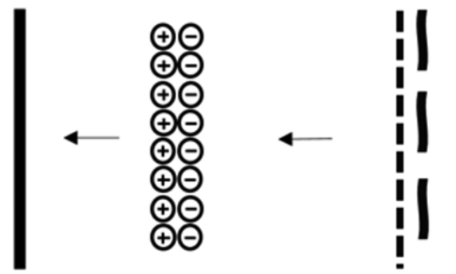

Figure 6. The flow chart of the preparation of ternary composite.

In 2011, Jaeseok Yi from Hanyang University, South Korea employed CVD-graphene sheets along with thin metal layers as the top electrodes of vertically aligned ZnO NRs (ZnO NRs-Gr/M), and studied the performance of this composite sensor [52]. The ZnO NRs-Gr/M hybrid structure could keep sufficient space between the whole nanowires to ensure rapid delivery of gas, as shown in Figure 7.

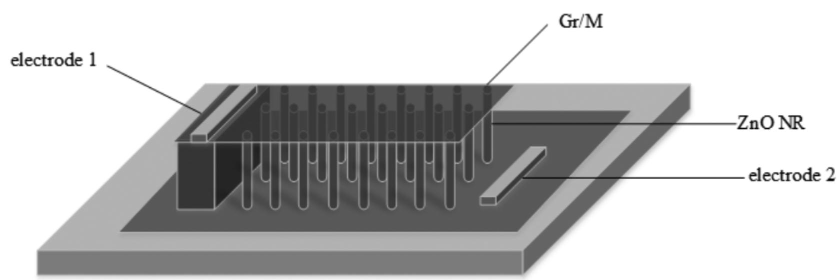

Figure 7. Schematic illustrating of the key steps for fabricating the ZnO NRs–Gr/M hybrid architectures [52].

3.1.4 Quaternary graphene-based Nanocomposite

To improve the sensing performance of graphene-based binary hybrids further, ternary or quaternary graphene hybrids have been developed in which noble-metal-metal oxide, noble-metal-conducting polymer or metal-oxide-conducting polymer was hybridized with graphene to combine their advantages. To combine the advantages of noble-metal and metal oxide, Pd-WO3 nanostructures were incorporated on RGO sheets using a controlled hydrothermal process to fabricate effective hydrogen-gas sensors; they exhibited a wide response range, good sensitivity, a rather low working temperature, a fast response and fast recovery time [53]. RGO provided carrier-transfer pathways, while Pd possessed high catalytic activity and consequently increased the reaction activity of the space-charge layers of WO3. In air, the oxygen molecules reacted preferentially with Pd, forming oxygen anions that then spilled over to the WO3 matrix. The target gases might be adsorbed onto the surface of Pd and then migrate to the surface of WO3 to react with surface oxygen species, thereby increasing the surface conductivity. Sensor arrays from multi-component, micro patterned NPs and graphene were developed by Nagelli et al. [54]; patterned noble-metal/metal-oxide-NPs on graphene were developed through region-specific plasma treatment followed by region-selective substrate-enhanced electro less deposition of AuNPs and solution alkalization of ferrous-chloride tetra hydrate in the presence of ammonia into Fe3O4-NPs. The patterned sensor arrays were highly selective for detecting low levels of chemical-vapor molecules at ppm levels.

Binary metal oxides have also been investigated to hybridize with graphene to enhance the sensitivity and the selectivity of gas sensing [55]. Cui et al. [56] synthesized Nano hybrids of indium-doped SnO2-NPs on an RGO surface prepared using a simple one-pot method at a relatively low temperature. The introduction of dopants facilitated NP nucleation on GO and improved the sensitivity and the selectivity, which could be attributed to the increase of oxygen species on the NP surface by introducing indium as a dopant and the differential selectivity of SnO2 and In2O3.

Besides the ternary hybrids, a new quaternary graphene-based hybrid has been synthesized from the assembly of magnetic NP-decorated RGO (Fe_3O_4/RGO) with PEDOT and PIL [57]. The Fe_3O_4/RGO/PIL/PEDOT sensor exhibited stable, reproducible signals at room temperature for both polar and non-polar VOCs. That quaternary hybrid demonstrated enhanced sensitivity, selectivity, signal-to-noise ratio and reduced response time compared to its elementary constituents, which suggested a positive synergy of properties through structuring the conducting architecture by spray LbL.

4. 1 Ammonia Sensing

Ammonia (NH_3) is a compound of nitrogen and hydrogen with the formula NH_3, which is a colorless gas with a characteristic pungent smell. Ammonia not only contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers, but also is a building-block for the synthesis of many pharmaceuticals, and is used in many commercial products. Although widely used, this gas is both caustic a hazardous, and thus it is harmful to human and would pollute environment. Therefore, the detection of NH3 is a pressing requirement for the modern society. Recently, a great deal of efforts had presented a great leap forward in the development of graphene gas sensors for ammonia detection. Gautam and his team investigated ammonia gas-sensing behaviors of graphene synthesized by CVD, of which the sensitivity and the recovery time were enhanced by the deposition of gold nanoparticles on the surface of graphene films [58-62]. Yavari et al. manufactured a device which was distinctly superior to commercially available NO_2 and NH_3 detectors [62-64]. They found graphene films synthesized by CVD had an outstanding property of detection of NO_2 and NH_3 at room temperature. The detection limits of both NO_2 and NH_3 reached to ppb level. Wu and his co-workers reported a contrast experiment between graphene/PANI nanocomposites, and PANI to explore their sensing properties [64-69]. The results indicated that the NH3 detection limit of graphene/PANI sensors (ca. 1

ppm) was lower than that of PANI (ca. 10 ppm). This indicated that the sensitivity of graphene/PANI sensors for NH_3 detection was enhanced by introduction of graphene into PANI. A simple, low-cost, and practical inkjet-printing technique for fabricating an innovative flexible gas sensor based on graphene–poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) composite films with high uniformity over a large area was created by Seekaew et al. [70-76]. Figure 8 clearly depicts a schematic diagram of this brand new gas sensor fabrication process. The ink-jet printed graphene-PEDOT: PSS gas sensor exhibited high response and high selectivity to NH_3 in a low concentration ranging from 25 to 1000 ppm at room temperature. This novel and convenient method would provide a new thought for the controllable and mass manufacture of gas detectors.

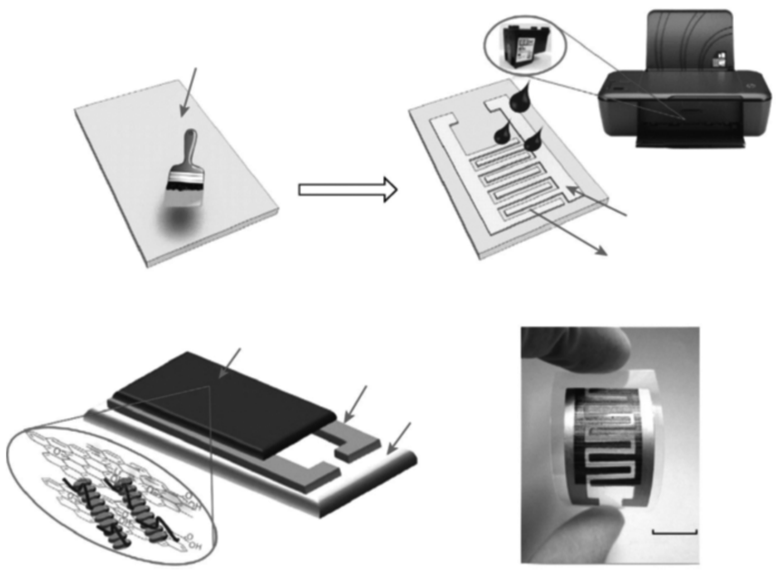

Fig. 8 Schematic diagram of gas-sensor fabrication process. [62]

4.2 Response Mechanisms of Gas sensing

We have given a brief introduction to the classification of gas/vapor sensors. Considering that the gas-sensing mechanisms of graphene is uncertain and related research is rare, herein, we just give a recognized point of view as a general introduction of the reference of other related literatures [76-79]. Graphene is intrinsically inert and nonselective. It's great efficiency to conduct electricity and distinguishing features of ballistic transport of charges decide that this two-dimensional material is an ideal candidate to serve as a platform or a supporter, in which we can realize many specific functions by doping or compositing with other materials. [80-89] Once combined with other materials physically or chemically, graphene can show the characteristics of the semiconductor in normal circumstances, of which conductivity is determined by carriers' concentration. For chemiresistor-type sensors, sensing materials show response to externalities by the change of conductivity, that is the variation of concentration of hole or electron carriers. [90-95]

Sometimes, p-type graphene and n-type graphene can transform from one to another by changing the annealing temperature. Wang et al. explored this interesting phenomenon that the slightly reduced p-type graphene showed ultrasensitive gas sensing at room temperature, with a response of 58 % to 1 ppm ethanol, while the graphene could become n-type and insensitive to gas sensing, with a low response of 0.5 % to 50 ppm ethanol, by simply increasing the annealing temperature to about 300 _C [95-100].

Conclusions

Improving the sensitivity of the sensor is the main goal of studying gas sensing. The excellent conductivity of graphene as well as the surface-rich and easily modifiable functional groups gives it great advantage as a resistance sensor. Pure graphene prepared by various methods generally responds well to gases with concentration below 5%. In recent years, graphene, polymer, metal and metal oxide composite obtained by the new composite materials emerge in the field of gas detection, and the response is up to 30%, which greatly enhances the performance, indicating that graphene composites in the gas sensitive material has a very good potential for development. At the same time, researchers have proposed many different sensors and reduced the production cost, such as vertical structure, graphene as a vertical electrode and so on, which is the foundation of the graphene sensor scale production.

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