3D Graphene-Based Toxic Gas Sensors

Subjects: Others

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Air pollution is becoming an increasingly important global issue. Toxic gases such as ammonia, nitrogen dioxide, and volatile organic compounds (VOCs) like phenol are very common air pollutants. To date, various sensing methods have been proposed to detect these toxic gases. Researchers are trying their best to build sensors with the lowest detection limit, the highest sensitivity, and the best selectivity. As a 2D material, graphene is very sensitive to many gases and so can be used for gas sensors. Recent studies have shown that graphene with a 3D structure can increase the gas sensitivity of the sensors. The limit of detection (LOD) of the sensors can be upgraded from ppm level to several ppb level.

Keywords: graphene ; graphene hydrogel ; graphene aerogel ; gas sensor

1. Introduction

There is a huge demand for the development of simple and reliable gas sensors [1]. In many fields, such as agriculture, medical diagnosis, and industrial waste, especially in environmental monitoring, it is necessary to detect NO_x (especially NO_2), ammonia (NH_3), and volatile organic compounds (VOCs), because of their possible toxicity and related risks to the ecosystem [2][3]. In many countries, air pollution is a major environmental problem caused by rapid industrialization. A large amount of NO_2 is emitted into the environment every year due to the industrial combustions and automobile emissions [4]. Therefore, the detection of NO_2 has aroused widespread concerns, because it is harmful to the plants and respiratory systems of people and animals [5]. Additionally, NO_2 can cause acid rain and photochemical smog [6][7]. Therefore, the United States Environmental Protection Agency (EPA) defines NO_2 as a typical air pollutant, and the exposure limit is only 53 ppb [8]. Ammonia (NH_3) is also a common dangerous air pollutant, which is produced by the industrial process, agricultural production, and manufacturing process [9][10]. Specifically, any overexposure to the high concentrations of NH_3 (>30 ppm, 10 min) can irritate the human eye, skin, and respiratory system [11][12][13]. VOCs are the hydrocarbons that exist as gases or vapor at room temperature, which can be emitted from numerous products and activities, e.g., detergents, paints, solvents, tools, clothes, toys, cleaning, and cooking [14]. Aldehyde, aromatic, aliphatic, halogenated, and terpenoid compounds are the VOCs commonly detected in commercial buildings [14][15]. Toxic VOCs that have been previously detected in air by any type of sensors include formaldehyde, acetaldehyde, benzene, toluene, xylenes, phenol, pyridine, acetone, acetic anhydride, carbon disulfide, dihydroxybenzene, and so on [14][15][16][17][18][19]. For example, phenol is a toxic VOC occurring both naturally but also from industrial processes, which can be rapidly absorbed through the skin and cause skin and eye burns upon contact [20]. It is considered as a serious pollutant because of the toxicity and persistence in the environment. The short-term exposure limit of phenol is 10 ppm, 60 min [21]. Because of the serious environmental pollution, phenol monitoring becomes an urgent problem. Therefore, with the monitoring development of air pollution, the demand for gas sensors will increase rapidly in the future.

As a 2D material, graphene has many advantages, such as large conjugated structure, high specific surface area, high conductivity, easy to be synthesized, sensitive to the gas molecules, and so on. It has been proven to be a promising high-performance gas detection material [22]. Graphene surface can easily absorb some molecules, such as NO_2, NH_3, CO_2, and so on. Moreover, the conductivity of graphene will change after adsorption of target gas molecules. The concentration of target gas in the environment can be detected by monitoring the change of conductivity. There have been many reports on the application of graphene in gas sensors, including pure graphene [23][24][25][26] and graphene composite materials [27][28][29][30][31]. There are many factors affecting graphene-based sensors, including: synthetic method [32][33][34], chemical structure [35][36][37], interlaminar structure [34][38], testing environment [39][40][41][42], and surface properties [43][44][45][46][47]. Due to the π-π accumulation and Van Der Waals force binding between graphene, the 2D graphene nanocomposites tend to agglomerate, resulting in the reduction of specific surface area [48][49][50]. In order to make full use of the characteristics of graphene, 2D graphene is usually assembled into a three-dimensional (3D) framework state by a series of methods. In contrast, due to the combination of 3D porous structure and the inherent characteristics of graphene, 3D graphene provides more space and larger surface area to transport and store electrons.

3D graphene has good conductivity, large specific surface area, and versatile gas adsorption sites. Furthermore, the defects and edge positions on the 3D porous graphene play an important role in promoting gas adsorption [48]. In recent years, compared with 2D graphene structures, 3D porous graphene structures such as graphene hydrogels, graphene aerogels, and graphene foams have been used as high-performance gas sensors [49]. Although 3D graphene has broad prospects in the field of gas sensors with the super high sensitivity, the selectivity is not satisfactory. Different gas molecules may adsorb on the same 3D graphene sheets and lead to the total change of the resistance [50][51]. It is difficult to quantitatively distinguish one target gas from a gas mixture. To improve the selectivity, defect engineering is generally needed to modulate graphene [52].

Several reviews have presented the main development of graphene-based gas sensors. For example, in 2015, Meng et al. [49] reviewed the graphene-based hybrids for chemi-resistive gas sensors. They focused on the sensing principles and synthesis processes of the graphene-based hybrids with noble metals, metal oxides, and conducting polymers. In 2018, Xia et al. [50] summarized the 3D structure graphene/metal oxide hybrids for gas sensors. They concluded a variety of logical strategies to design the 3D nanohybrids of RGO and MOx. In 2020, Ilnicka et al. [51] summarized the graphene-based hydrogen gas sensors, a special case of gas sensitivity to H_2. However, the above reviews did not reflect the whole progress of graphene gas sensors, especially for the air pollution monitoring applications. This paper aims to summarize the recent progress of the gas sensors based on 3D graphene frameworks in the detection of air pollutants.

2. Synthesis of 3D Graphene Frameworks

Graphene oxide (GO) and reduced graphene oxide (RGO) have a 2D conjugated structure with single-atom thickness and residual oxygen-containing groups, which can be regarded as 2D conjugated macromolecules, structurally. They have rich chemical activities, which are helpful for 3D self-assembly through a series of chemical modification methods to regulate the interaction between the layers [34][38].

Graphene hydrogel is one of the major 3D assemblies. Chemically modified graphene (CMG) hydrogels prepared from GO or RGO can be used for large-scale production. As shown in Figure 1, RGO hydrogels (RGOHs) can be obtained by the following methods:

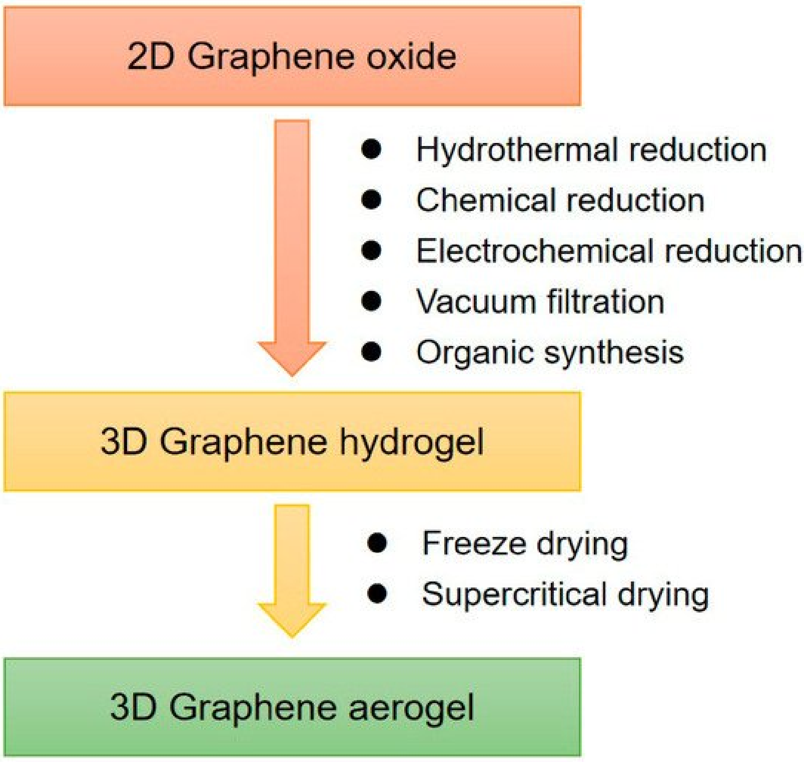

Figure 1. Synthesis methods of 3D graphene frameworks.

(1) Hydrothermal reduction, which is simple, fast, and free of impurities. At present, the commonly used hydrothermal method is to prepare RGO dispersion by hydrothermal treatment at 180 °C [53][54][55].

(2) Chemical reduction, which is beneficial for large-scale production, and various reducing agents can be selected [56][57][58][59][60][61][62][63][64][65].

(3) Electrochemical reduction [66][67][68]. The hydrogel prepared by this method is applied to the electrode surface and can be directly applied to the electrode materials of electrochemical instruments.

(4) Vacuum filtration. A simple vacuum filtration method was developed to prepare RGO hydrogels with high conductivity, anisotropy, and responsive stimuli [69][70].

In addition to the 3D self-assembly of graphene in a water system, the assembly of the graphene in an organic system can also be achieved by thermal solvent reduction [71][72][73].

Graphene aerogel composites are usually prepared by supercritical drying or freeze-drying of hydrogel precursors [74][75]. For example, highly compressible RGO aerogels can be obtained by freeze-drying and microwave treatment. Directional freezing is a well-known processing technology of porous materials. This technology can also be used for the preparation of graphene aerogels [76]. Moreover, the controllable heat treatment technology can also reduce GO to RGO and restore conductivity. The regulation of the chemical structure of GO can adjust the morphology and elasticity of aerogels, for example, the oxygen functional groups in GO have a significant effect on the morphology and elasticity of the gels [77].

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