Review

Progress in graphene-based materials as superior media for sensing, sorption, and separation of gaseous pollutants

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ABSTRACT

Rapid population growth accompanied by industrialization and urbanization has led to a noticeable degradation of air quality. There is a strong need to appraise novel materials for the treatment of diverse pollutants in the atmosphere. Among them, graphene oxide (GO) is envisaged as one of the most promising layered materials with expansive applicability in numerous fields, especially in the pollutant removal processes, due to many uniquely advantageous features (e.g., tunable physical properties, excellent thermal stability, electrical conductivity, exceptionally high surface area, and pore volume). In the last decade, researchers have also put much efforts to produce graphene-based composites through the fabrication of graphene or GO with a variety of materials such as carbon nanotubes, metallic nanoparticles, metal-organic framework, and polymers. Because of the advanced features (e.g., strong mechanical and anti-corrosive properties, stimuli responsive property, and high porosity) of graphene-based composites, they have been used preferably for air quality management (AQM) through adsorption, separation, and sensing of gaseous pollutants. In this comprehensive review, we offer a contemporary state of the art discussion on using graphene-based composites for AQM purposes. The nature of the interactions between composites and various types of gaseous pollutants has hence been reviewed in various respects. To expedite further research and development on this topic, we take into consideration the technical challenges with suggestions for the directions of relevant future research.

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1. Introduction

The continuous advancement of industry and agriculture has enhanced production and emission of potentially toxic and combustible gases into the atmosphere. A variety of gaseous compounds including oxides of nitrogen and sulfur, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) are often identified as highly detrimental to pose human health risks. These gases can be formed by natural origins (like ultraviolet photochemical processes and microbiological processes) as well as various man-made sources (e.g., vehicles, furnaces, stoves, and electric power plants) [1,2]. Thus, for the purpose of AQM, the development of highly sensitive, selective, and lucrative materials for sorbents/catalysts and sensors is in great demand to effectively remove those pollutants and to accurately monitor their behavior, respectively.

Current research efforts strived to understand the potential utility of novel materials in the field of AQM. For instance, physisorption in advanced, tunable porous media is regarded as one of the most reliable approaches for the separation and removal of gaseous pollutants including VOCs. Consequently, many attempts have been made to synthesize an extensive variety of modified porous materials (e.g., polymers, metal-organic frameworks (MOFs), zeolites, and covalent organic frameworks) for removing, sensing, or separating gaseous pollutants [3–8].

Among the aforementioned materials, graphene and graphene oxide (GO) have been considered as a proficient matrix for sorption and sensing of gaseous pollutants due to their advanced properties (e.g., facile synthesis method, high surface area, robust pore structure, light-weight, high chemical stability, and high thermal stability) [9,10]. Moreover, the findings of various advantageous properties (e.g., surface moieties, high water dispensability, and hydrophilicity) support the potent role of GO as an excellent contender in many other fields of applications (e.g., fabrication of a super capacitor and other nano materials) [11–13].

Graphite is the main ingredient for the production of graphene, GO, GO nanosheets, reduced GO (rGO), and other GO composites (e.g., GO/polymer composite and GO/MOF composites). On a comparatively large scale, various graphene-based materials can be prepared from graphite precursors through oxidation, exfoliation, and reduction [14–16]. As such preparation steps can yield many defective sites on the graphene, the resulting product is advantageous for sorption and sensing of gases and additional functions. Graphene can thus be used as an effective platform for engineering a wide variety of functions and for chemical modifications due to its largely expanded and tunable layer structure. The electrostatic interaction of GOs with the adsorbate also make them materials of interest for the sorption of various charged species [17].

Appropriate incorporation or combination of GO with other materials like polymers [18,19], nano particles [20], carbon nanotubes [21], and MOFs [22] gave rise to hybrid composites that combine advantageous properties of respective building blocks for extensive expansion of their application fields. For example, nanoporous graphene-polyoxometalate (GPOM) hybrid structures were synthesized by in-situ hydrazine hydrate reduction of GO with the use of phosphomolybdic acid as a cross-linker. As such, the polynuclear metal-oxo structured polyoxometalate provided a versatile building block cluster for the construction of functionalized hybrid materials. The ordered pore of GPOM exhibited a comparatively large specific surface area (e.g., 680 m²/g) that is ~30 to ~85 times greater than those of GO (23 m²/g) and POM (8 m²/g), respectively [23]. In addition, the MOF (HKUST-1)-GO composites showed enhanced porosity relative to the parent material (e.g., with the addition of GO up to 20% by weight). Indeed, when high amounts (e.g., more than 20%) of GO are dosed, the number of functional groups on the distorted graphene layers exceeds the active sites present in MOF with which they can interact. Accordingly, after drying, such excess layers of GO were seen to restack. Thus, restacked GO layers remained as agglomerates which led to further reduction in porosity [24].

Numerous review articles on graphene-based materials had been reported to describe their potent role in optical [25], electronic [16], electrochemical [26], and photocatalytic applications [27]. However, because of a paucity of information on their interactions with various gaseous pollutants, there is a strong demand to explore the kinetics and mechanisms behind the adsorption/sensing of GO and GO-based materials against various toxic gases or vapors including NO₂, Cl₂ toxic vapors, benzene, ammonia, sulfur volatiles, and so forth [28–34]. In sorptive removal of gaseous pollutants, various factors (like breakthrough volume, analyte concentration, and sorbent structure) need to be investigated thoroughly. Likewise, selectivity of sensor material is crucially important for practical application. A comprehensive study is thus desirable to investigate whether a graphene-based material could satisfy various criteria established for AQM applications. To address such issues, we conducted a critical survey of the experimental findings on GO-based materials for sorption, sensing, and separation of pollutant gases, with emphasis on volatile organic compounds and a brief discussion of their health risks. Then, we address their practical applicability for future research in AQM fields.

2. Properties of graphene oxide

GO is an oxidized structure of graphene exhibiting a high density of oxygen-containing functional moieties including hydroxyl, carbonyl, carboxyl, and epoxy in its lattice. GO can be synthesized economically by simple chemical oxidation (e.g., from graphite to graphene oxide) followed by exfoliation. Generally, Hummer's method (or modified Hummer's method) based on a combination of H₂SO₄ and KMnO₄ has been used for the preparation of graphene oxide. In Hummer's process, the reaction of KMnO₄ with H₂SO₄ produces a dimanganese heptoxide ion, which acts as an active species. As the bimetallic heptoxide is much more active than monometallic tetraoxide, the former is discharged when heated