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Review

Gas sensors using carbon nanomaterials: A review

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ABSTRACT

Carbon nanomaterials have been attracting a great deal of research interest in the last few years. Their unique electrical, optical and mechanical properties make them very interesting for developing the new generation of miniaturised, low-power, ubiquitous sensors. In the particular case of gas sensing, some carbon nanomaterials such as nanofibres, nanotubes and graphene are threatening the dominance position of other well established (nano)materials, yet the commercial exploitation of carbon nanomaterials is still a way off. This paper reviews the state of the art for electrical gas sensors employing carbon nanomaterials, identifies the bottlenecks that impair their commercialisation and also some recent breakthroughs. Finally an outlook in which challenges and opportunities are identified is given.

Contents

1. Introduction

In the last few years there has been an explosion in the number of published papers dealing with nanomaterials for gas sensing. There is a need for simple, sensitive and stable electronic sensors suited for trace detection in a wide spectrum of applications ranging from lab-on-a-chip and in vivo biosensors to environmental monitoring and warfare agent detection, as opposed to the often employed expensive, bulky and complicated instrumental methods. This need for inexpensive, low-power devices is fuelling the exponential growth of research in this area. Among the different nanomaterials one could consider for developing a gas sensor, carbon nanomaterials have been attracting a great deal of interest. Carbon materials with inherent nanoscale features have potential for becoming ideal components for the next generation of autonomous sensor technology, since they combine excellent detection sensitivity with interesting transduction properties in a single layer of material [1]. Low-dimensional carbon structures have most of their atoms exposed to the environment and, therefore, offer high specific surface area, which is advantageous for achieving high sensitivity. Unlike in polycrystalline materials (e.g. polycrystalline metal oxides), quasi-one dimensional materials avoid grain boundary poisoning, which improves the long-term stability of devices. Some carbon nanomaterials such as carbon nanotubes or graphene have high quality crystal lattices and show high carrier mobility (e.g. ballistic charge transport) and low noise.

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While the last two characteristics are important for getting good transduction properties, the surface chemistry of low-dimensional, high-quality crystal structures is, in principle, easier to understand and control than that of polycrystalline structures. In that sense, single crystalline nanostructures are good model materials for running computational chemistry studies, from which insight can be gained into their gas sensing mechanisms. The sensitivity and selectivity of carbon nanomaterials can be engineered by employing different techniques both to create defects and graft functional groups to their surface in a controlled way. Fabricated by different methods, carbon nanomaterials are often amenable to making devices by employing conventional methods such as lithography, which helps keeping costs low. Additionally, their mechanical properties make them suitable to become integrated in flexible electronic devices. They offer high sensitivity to cost ratio, even when operated at room temperature. Their low power demands make them good candidates for being operated remotely. The electronic signal transduction (e.g. a resistance change) of chemical environmental analytes is advantageous over optical methods, owing to lower cost, increased device simplicity, higher sample throughput and better portability.

This paper reviews the carbon nanomaterials that could integrate the new generation of gas sensors with superior performance and critically discusses their strengths and weaknesses. An overview on the different gas sensitive devices constructed employing such nanomaterials is given and the main technological barriers are identified. Finally, in an outlook on how the field may evolve in the next few years is given.

2. Carbon nanomaterials

In the last few years, carbon nanotubes have become the most studied carbon nanomaterial for developing gas sensors. Nowadays, graphene, a more recently studied allotrope of carbon, is challenging the dominance of carbon nanotubes. But carbon nanomaterials are not limited to nanotubes and graphene. They also exist as nano-particles, diamonds, fibres, cones, scrolls, whiskers, graphite polyhedral crystals and nanoporous carbon.

Part of the reason for the explosion of interest from the gas sensor community in carbon nanomaterials is that while ranging from well-defined nanosized molecules to tubes with lengths of hundreds of microns, they do not exhibit the instabilities of other nanomaterials as a result of the very high activation barriers to their structural rearrangement. As a consequence, they are highly stable even in their unfunctionalised forms. Despite the wide range of carbon nanomaterials possible, they exhibit common reaction chemistry: that of organic chemistry.

Before we review the use of carbon nanomaterials in electrical gas sensors, a short discussion on the properties and main fabrication techniques for some of these materials is given in this section.

2.1. Carbon black

Carbon black [C.A.S. No. 1333-86-4] is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its physical appearance is that of a black, finely divided pellet or powder. Two carbon black manufacturing processes (furnace black and thermal black) produce nearly all of the world's carbon blacks, with the furnace black process being the most common. The furnace black process uses heavy aromatic oils as feedstock. The production furnace uses a closed reactor to atomise the feedstock oil under carefully controlled conditions (primarily temperature and pressure). The primary feedstock is introduced into a hot gas stream (achieved by burning a secondary feedstock, e.g., natural gas or oil) where it vapourises and then pyrolyses in the vapour phase to form microscopic carbon particles. In most furnace reactors, the reaction rate is controlled by steam or water sprays. The carbon black produced is conveyed through the reactor, cooled, and collected in bag filters in a continuous process. Residual gas, or tail gas, from a furnace reactor includes a variety of gases such as carbon monoxide and hydrogen. Most furnace black plants use a portion of this residual gas to produce heat, steam, or electric power [2].

The thermal black process uses natural gas, consisting primarily of methane or heavy aromatic oils, as feedstock material. The process uses a pair of furnaces that alternate approximately every five minutes between preheating and carbon black production. The natural gas is injected into the hot refractory lined furnace, and, in the absence of air, the heat from the refractory material decomposes the natural gas into carbon black and hydrogen. The aerosol material stream is quenched with water sprays and filtered in a bag house. The exiting carbon black may be further processed to remove impurities, pelletised, screened, and then packaged for shipment. The hydrogen off-gas is burned in air to preheat the second furnace [2].

Carbon black is chemically and physically distinct from soot and black carbon, with most types containing greater than 97% elemental carbon arranged as aciniform (grape-like cluster) particulate. Carbon black is available with surface areas that are higher than 1000 m^2/g, particle size lower than 50 nm, and density much lower than the theoretical value for graphite (2.25 g/cm^3). Fig. 1 shows high-resolution TEM images of carbon blacks.

2.2. Carbon nanofibres

Vapour grown carbon nanofibres (VGCNF) are nanosized carbon fibres formed at catalytic metal particle surfaces (Fe, Ni, Co) in hot (900–1500 °C) hydrocarbon gases [3,4]. They are hollow. An initial filament is formed composed of well-organised graphitic planes lying in the "stacked-cup" morphology with diameters of 20–60 nm. The fibres can then be thickened by the deposition of an outer chemical vapour deposition layer, consisting of undulating graphitic planes which lie parallel to the fibre surface with some sp^3-hybridised carbons also present [5]. Many fibre grades are available with diameters averaging from 60–70 to 200 nm or more and as-formed lengths from 1 to 100 mm.

Alternatively, carbon nanofibres can be produced at low cost and with various controlled structures at relatively high rates [6–8] employing electrospinning. A polymer such as polyacrylonitrile (PAN) is used as carbon source. The polymer is mixed and stirred with a suitable solvent with low boiling point and sufficiently high conductivity for electrospinning to obtain a polymer solution. The polymer solution is ejected from a syringe tip onto a rotating collector. A voltage (typically few kV) is applied between the syringe tip and the collector, which are kept a few cm away. The electrospun materials are stabilised by undergoing an annealing in air at temperatures ranging from 300 °C to 400 °C for a few hours. Finally, a carbonisation step is performed by calcinating the sample at temperatures ranging from 700 °C to 1000 °C in the absence of oxygen (e.g. in N_2 or Ar). Employing this method, carbon nanofibres of 40–400 nm in diameter and above 70 μm in length can be obtained [8–10] (see Fig. 2).

2.3. Carbon nanotubes

The allotropes of carbon include diamond in which carbon atoms are bonded together in a tetrahedral lattice arrangement, graphite where the carbon atoms are bonded in sheets of a hexagonal lattice, graphene (single sheets of graphite), and fullerenes in