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A Review of hybridization of carbon nanotube into graphene for gas sensor application

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Abstract Hybridization of two mechanically strong materials which is carbon nanotube and graphene can provide specific advantages over other materials in gas sensor research and can relate to the chemical properties. Consequently, graphene and carbon nanotube show extreme sensitivity towards changes in the local chemical environment that originates from the susceptibility of the electronic structure to interacting molecules. Furthermore, a sensitivity and chemical selectivity to a diverse array has made them perfect candidates for consolidation into the design of gas sensor. The development of hybridization of carbon nanotube and graphene based gas sensor still in its infancy, but attempts to make the gas sensor more quantitative are important for further advancement of gas sensor innovation.

1. Introduction

The atmospheric air, there are various kinds of chemical species that are common and manufactured. Some of which are crucial to our daily life while many others are harmful. To response the changes in the local chemical environment, the researchers have been looking for affordable alternatives to obtain a better gas sensor.

Basically, there are various kinds of gas sensors so far developed. Gas sensors, which have been in incredible interest to make sure safety, health, environmental reservation, energy saving and others. In order to be utilized in practice, gas sensors should fulfill many requirements which depend on the purposes and condition of sensor operation. Among the requirement, the important would be sensing performance such as sensitivity, selectivity, rate of response and recovery rate in the chemical environment. Furthermore, there is also a strong demand for the ability to monitor and control the ambient environment, especially with the increasing concern of the global warming.

The key importance in research and development of gas sensors is the sensing materials. Advance progress in the synthesis and fundamental understanding of surface phenomena has produce extraordinary favor about formation of nanomaterials into sensor design [1]. Nanomaterial sensor is needed to serve as a cheap, small, users-friendly and reliable gas sensing device [2].

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More recently, carbon based materials called Carbon Nanotubes (CNTs) and Graphene have been identified to be promising sensing material due to their unique and excellent electrical properties and mechanical properties. Besides, there have a low operation temperatures compared with other gas sensors. The gas sensing mechanism generally attributed to the adsorption and desorption of gaseous molecules on the surface, leading to changes in the conducting properties. The unique structures and outstanding electronic properties of CNTs and Graphene which are small size, large specific surface area, high electron mobility and high sensitivity to electrical perturbations from gas molecules [3].

2. Graphene

Carbon is one of the essential building blocks of life on earth and is the 15th most abundant element on earth and the 4th most abundant in the universe. Since Iijima discovered CNTs in 1991 [4], the research and development by utilizing carbon based material has got a superb attention. The world has more valued this carbon material when the duo from the Manchester University successfully created the wonder material called graphene in 2004 using the scotch-tape mechanical exfoliation technique.

Graphene consists of two-dimensional array of carbon atoms covalently attached via sp^2 bonds to produce a honeycomb sheet. Crystal structure of graphene consists of hexagonal rings forming thin parallel plates. The outermost electron shell of a carbon atom has four valence electrons, three of it are used by the covalent bonds. The graphene are tied together by weak van der Waals forces. The graphene layer structure allows sliding movement parallel graphene plates. Weak bonding between the plates determines softness and self-lubricating properties of graphite [5]. Figure 1 shows the graphene structure (Figure (a)) and the SEM image (Figure (b)) seen randomly aggregated wrinkled sheets closely associated with each other.

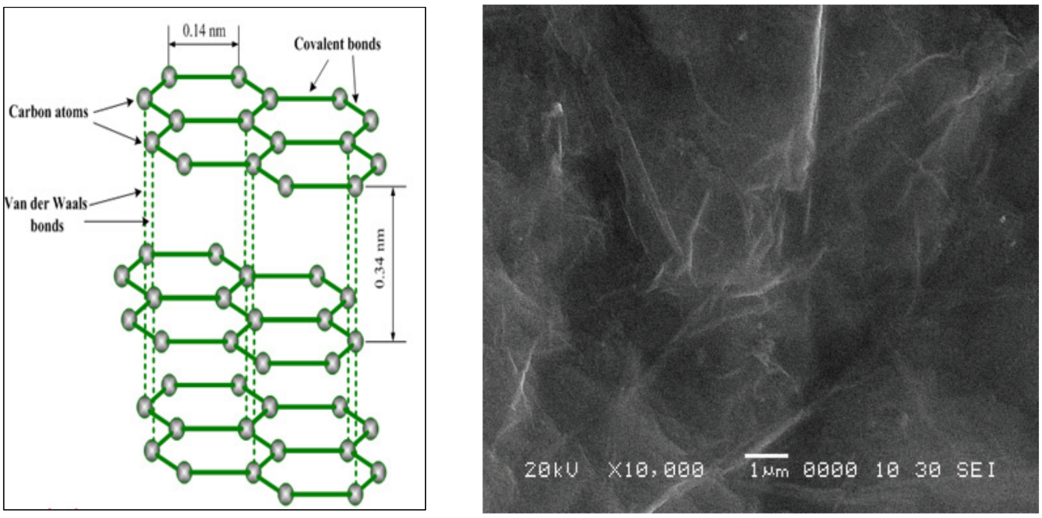

Figure 1. (a) Graphene structure [5]. (b) SEM micrograph of Graphene Oxide (GO) [17]

According t (a) n Choudhuri, et al. [18] graphene sheet ‘Bulk Synthesis of Graphene Nanosheets’, GO was synthesized by using the Modified Hummers method. This method can produces cheap and large quantities of graphene as well as easy to manipulate for device fabrication. Modified Hummers method yielded a graphene oxide. The oxide group oxygen and hydroxyl come from a chemical reaction between mixtures of concentration acid with an oxidation agent by a heat process. A freestanding graphene presented the possibility of high sensitivity towards detection of chemical analytes. Graphene is shown to exhibit inherently low electrical noise at room temperature and high electron mobility [12].

3. Reduced Graphene Oxide (rGO)

The oxidation process is to decrease or losing the electron, while the reduction process is increase or gaining the electron. Figure 2 shows acronyms for oxidation and reduction process [7]. According to V. H Pham et al. (2012) [6] graphene sheet 'Chemical reduction of an aqueous suspension of graphene oxide of nascent hydrogen' concentration between of aluminium foil (Al foil) and acid chloric (HCl), Al foil, sodium hydroxide (NaOH) and Zink (Zn) powder and NaOH are used to reduce GO. This method is simple and effective that known as nascent hydrogen. Figure 3 shows SEM image of rGO deposited on silicon substrate.

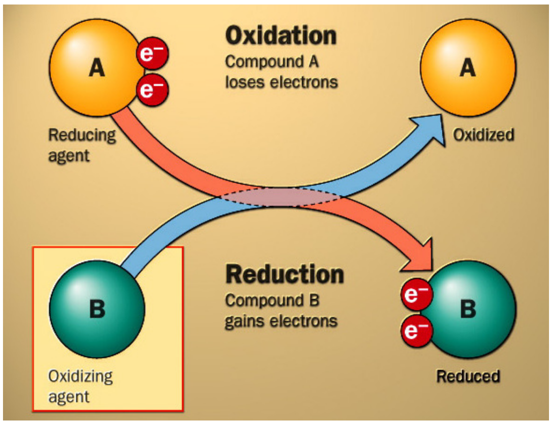

Figure 2. Basic oxidation and reduction [7]

Others metal can be used to reduce GO such as iron (Fe), magnesium (Mg) and manganese (Mn) for this reason of nascent hydrogen that can produce a metal surface based on the solution of oxidation [6]. The higher is the pH of GO suspension, the larger is the zeta potential of GO as a function and the electrostatic force among GO sheets [6]. If the electrostatic force among GO sheets is greater than or equal to the total of gravity and van der waals force, the GO hydrosol can be stabilize forever. SEM images of the rGO deposited by spin coating on a silicon substrate reported in figure. Some overlapping of flakes is noticeable [16].

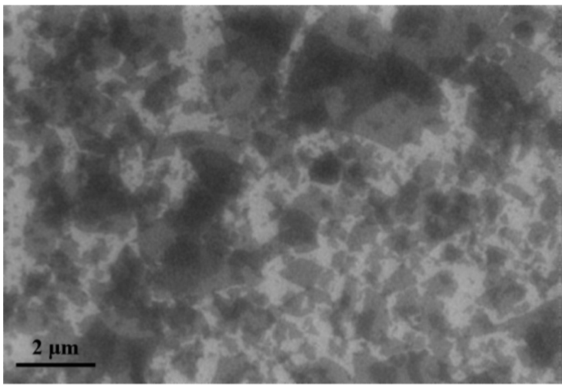

Figure 3. SEM image of rGO deposited on silicon substrate [16]

The electronic properties of graphene have been found to be extremely sensitive to the local chemical environment. Reduced graphene oxide has also been reported as a useful material for developing gas sensor. The first study of graphene use in gas sensing was reported in 2007 by Novoselov's group. The adsorption of ppm of gases caused the gas sensor to show concentration-dependent changes in resistivity.

4. Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are another nanoscale allotrope of carbon. They can be thought of as ribbons of graphene that have been rolled into a tube. While only nanometers in diameter, CNTs can grow onto millimeters in length. Due to the strength of the bonds in a hexagonal carbon lattice, nanotubes are one of the strongest fibers ever discovered. Primarily, CNTs are divided in two different types, determined by the number of the walls of the nanotube either Single Wall Nanotube (SWNT) or Multiwall Nanotube (MWNT) [15].

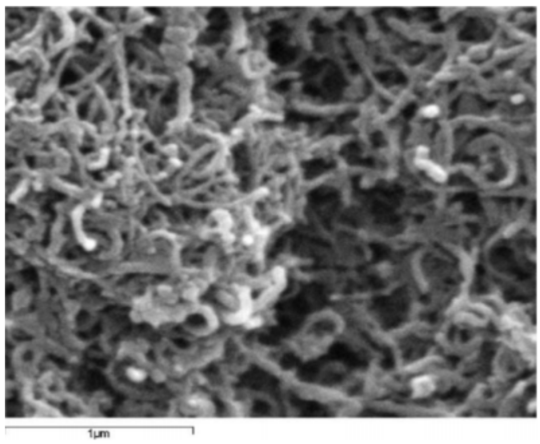

Figure 4. SEM image of CVD grown multiwall CNT bundles [19]

Figure 4 shows SEM image of CVD grown multiwall CNT bundles. The image shows CNTs appear randomly oriented in the form of a porous mat [19]. CNTs possesses exceptionally high surface to volume ratio. These characteristics lead the CNTs a strong and promising candidate for high sensitivity gas sensor [15]. Dong *et al* [13] used carboxylic acid functionalized CNTs for detection of 10 ppm carbon monoxide (CO) gas through weak hydrogen bonding with the attached carboxylic group. Recently, CNTs based electronic gas sensor either in the form of chemiresistors or back-gated field-effect transistors have been created to detect various gases [12]. In the sensing process, basically CNTs accept electrons in the sensing. The response times of CNT is mainly governed by the generation of the charge carriers in the defect sites and depends on how fast these carriers can be transported from the defect sites to the electrodes [12]. Sensor conductance was investigated in the presence of nitrogen dioxide and ammonia vapors [19]. Figure 5 shows the electrical response of SWCNT device to gas molecules.

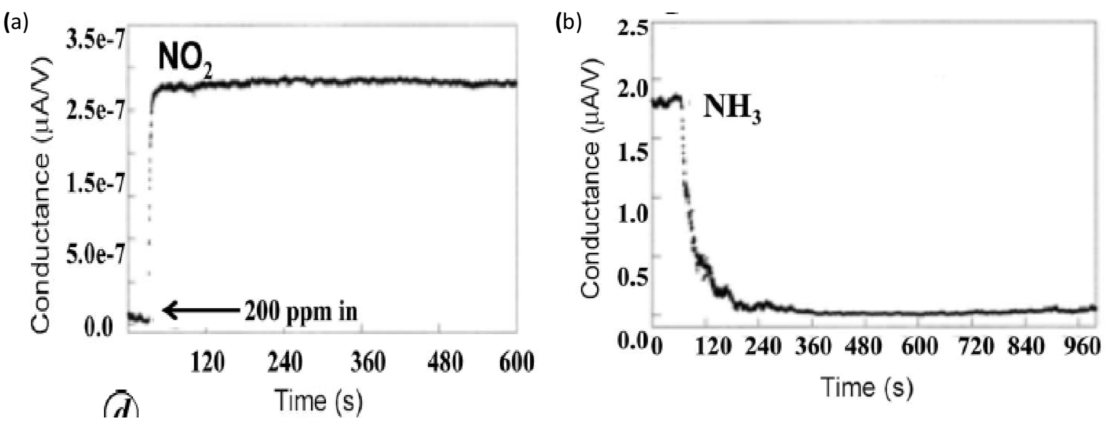

Figure 5. Conductance versus time response for 200 ppm NO_2 and 1% NH_3 exposures respectively [19]

5. Hybridization carbon nanotube (CNTs) and graphene gas sensor.

An advanced carbon based gas sensing material consisted of CNTs and graphene hybrid film were introduced. These intelligent and unique graphene-carbon nanotube consist of CNTs connected perpendicularly to graphene layers, could overcome some of the shortcomings and limitations of individual components [8-10]. The hybrid CNTs and graphene structure potentially shows outstanding properties that could not be attained either material alone.

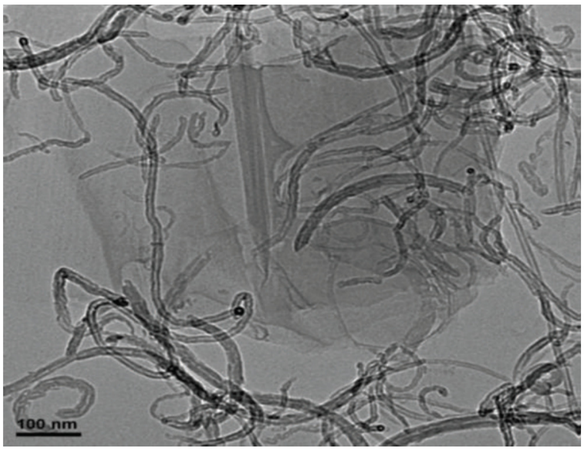

Figure 6. TEM micrographs of G-MWCNTs [17]

Report indicated that the chemically bonded graphene leaves on CNTs show good optoelectronic and gas sensing properties with reduced sheet resistance [14]. Gas molecules concentration dependence of electrical property was analyzed and the sensor will proposed based on carrier transportation and adsorption isotherm respectively for different gas molecules. Variety of gas sensors have been proposed to detect different types of chemical gas molecules such as Nitrogen Dioxide (NO_2), Ammonia (NH_3), Methane (CH_4), Hydrogen (H_2), Hydrogen Sulphite (H_2S) and Oxygen (O_2). TEM images of G-MWCNTs hybrids are shown in figure 6. As observed from the micrograph, the MWCNTs are seen to

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be incorporated into graphene layers and the surface morphology exhibits a mixed structure with MWCNTs dispersed between different GO sheets [17].

The gas sensitivity (S) was determined by $S = (R-R_0) / R_0$, where R_0 is the initial resistance value measured in the pure gas and R is the resistance value measured in the presence of gas mixture. Figure 7 shows NO_2 sensing response signal from CNTs/rGO hybrid film devices operated at room temperature. The results shows, CNTs/rGO hybrid films take advantage of the high sensing performance on NO_2 gas. CNTs/rGO gas sensor responded to 10 ppm NO_2 at room temperature with a sensitivity of 20% after 60 minutes of exposure [20].

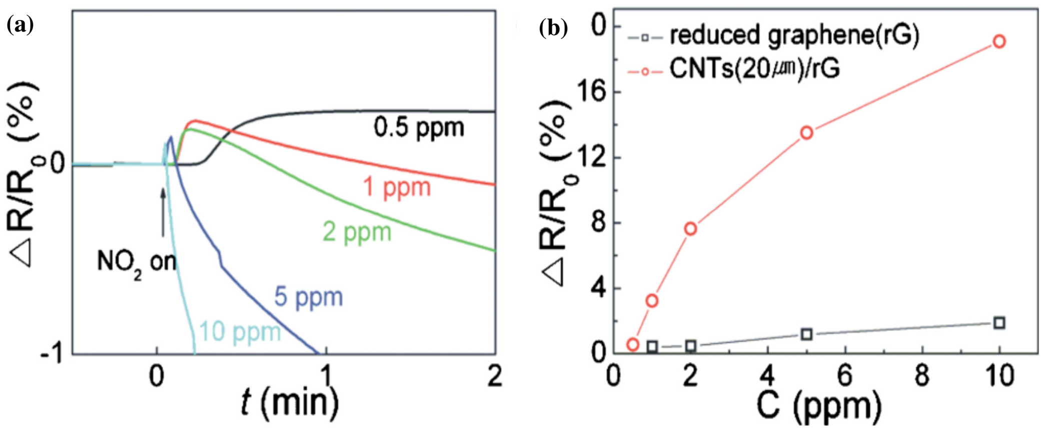

Figure 7. (a) NO_2 sensing behaviours of CNTs/rGO hybrid film devices at NO_2 concentrations from 0.5 – 10ppm. (b) Resistance response of rGO/CNTs [20]

6. Gas sensor array

An array module containing different types of gas sensors to sense the gases. If the target gas was assorted with other gases, the gas sensor array containing different sensors was more efficient when measuring a specific gas than a single element [11]. Another capability of the gas sensors is the sensors can be manufactured to be very small. In addition, portability and low power consumption are important characteristics needed for this application. GO was used to spin coat a Si substrate and standard photolithography was used to create interdigitated arrays of Ti/Au electrodes [19]. Liu and co-workers [21] to decorate RGO with Pd nanoparticles via a solution chemistry method. An array of sensors using oxygen plasma treated multiwalled CNTs decorated with Pd nanoparticles [22]. Figure 8 shows typical room temperature responses of the sensors to H_2S.

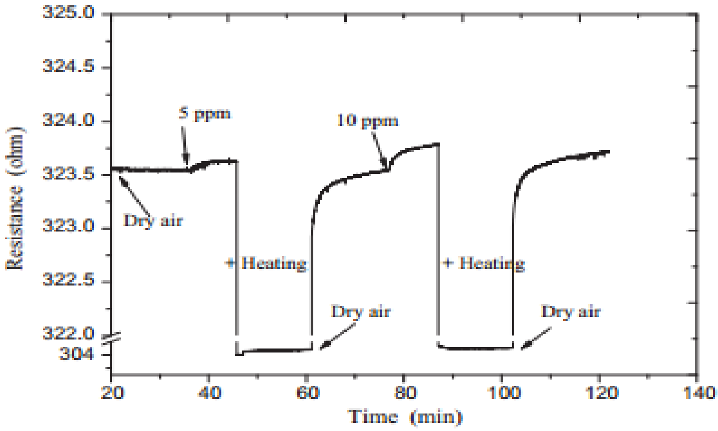

Figure 8. Response and recovery of a Pd-CNT sensors towards H_2S. Sensor respond at room temperature and heating at 150℃ is applied during initial phase of recovery to promote desorption of gas species [22]

7. Conclusion

The unique properties of graphene, reduced graphene oxide and CNTs offer various advantages and threatening the dominance of established nanomaterials in potential application of gas sensors. In this review, selectivity and sensitivity remains an important issue as many studies show the difficulty of making carbon nanomaterial absolutely selective and sensitive for different gas. CNTs and graphene sensors provide high sensitivity up to sub ppb level for a range of gases a room temperature. Hybridization of graphene and CNTs is considerably extending the possibilities of gas sensing. They presented possibility of high sensitivity towards detection of chemical analytes. Portable sensor arrays technology lies in the development that allow detecting and screening multiple analytes gas. Improved modification methods are being investigated and developed for hybridization of graphene CNTs sensor.

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