

Applications of Graphene: Supercapacitors and Gas Sensors

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Abstract. This paper provides a comprehensive overview of the unique physical and chemical properties and structures of graphene. It delves into the exceptional electronic and mechanical properties of graphene that make it a promising material for various applications. The paper particularly focuses on the use of graphene in supercapacitors and sensing techniques, specifically gas sensors. In the realm of energy storage, the paper elucidates how the high surface area and excellent conductivity of graphene contribute to the superior performance of graphene-based supercapacitors. It further explores the mechanism of charge storage in these devices, highlighting the role of pore sizes in graphene sheets on capacitance. In the context of gas sensors, the paper discusses how the sensitivity of graphene's electronic properties to its surrounding environment enables its use in detecting different gases. The paper concludes with a discussion of the challenges and future prospects in harnessing the potential of graphene in these applications.

1. Introduction

Graphene, characterized as a single layer of carbon atoms meticulously arranged into a two-dimensional (2D) honeycomb lattice, serves as the fundamental constituent for all other graphitic materials, irrespective of their dimensionalities (Figure 1) [1,2]. This unique configuration arises from each carbon atom in graphene covalently bonding to three other carbons, thereby forming a hexagonal pattern. One valence electron from each carbon atom is delocalized, free to traverse the entire plane, which significantly contributes to graphene's exceptional electrical conductivity.

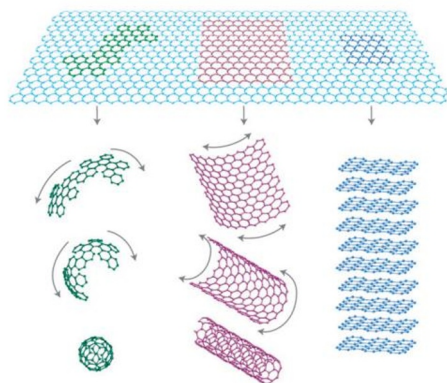


Fig. 1. Graphene: mother of all graphitic forms from Rao et al. [2]

One of the most salient properties of graphene is its unparalleled strength. It exhibits remarkable robustness, approximately 200 times that of steel, attributable to the covalent bonding between its carbon atoms. Despite its formidable strength, graphene retains a high degree of

flexibility, capable of enduring bending, twisting, and stretching without succumbing to fracture.

In addition to its robustness and flexibility, graphene demonstrates superior conductivity, both thermally and electrically. Its electrical conductivity outstrips that of copper, and its thermal conductivity surpasses all other known materials. These attributes render graphene a promising candidate for a myriad of applications, particularly in the realm of electronics. Another intriguing property of graphene is its near-complete transparency. It absorbs a mere 2.3% of the incident light, a characteristic that renders it advantageous for applications in optoelectronics. Moreover, graphene exhibits impermeability to all gases and liquids, establishing it as an excellent barrier material.

Over the past decade, extensive research at the laboratory scale across disciplines such as physics, chemistry, materials science, engineering, and biology has positioned graphene as a material of significant potential for industrial applications [3]. Its superior strength, flexibility, and conductivity, coupled with its transparency and impermeability, make it a potential candidate for a multitude of industrial uses. For instance, in the electronics industry, graphene could revolutionize the development of devices by enabling faster, thinner, and more flexible components. Similarly, in the energy sector, graphene's impressive electrical conductivity and large surface area could enhance the efficiency and capacity of energy storage devices including batteries, supercapacitors, etc. The advancement of novel energy storage systems (ESSs) that exhibit high performance and are apt for the forthcoming generation of intelligent electronics and electric vehicles constitutes one of the most pivotal fields of study [4].

Moreover, the study of graphene's industrial applications extends to the realm of composite materials.

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The incorporation of graphene into composites can significantly enhance their mechanical, thermal, and electrical properties, opening up new possibilities for industries such as aerospace, automotive, and construction. However, realizing the full potential of graphene in these applications requires overcoming challenges in its synthesis and production at an industrial scale, as well as understanding its interaction with other materials. These challenges underscore the importance of continued research and development in graphene technology, which will not only advance our scientific understanding but also drive innovation and progress in various industries.

In the contents below, two specific industrial implications in energy storage and gas sensors will be discussed more deeply.

2. Use of graphene in supercapacitors

2.1 Structure and mechanism of supercapacitors

A supercapacitor is a high-capacity capacitor that stores energy through two storage principles: electrochemical pseudocapacitance and static double-layer capacitance. Both principles collectively influence the total capacitance of the supercapacitor, with the proportion of the two being contingent upon the design and composition of the electrodes. A supercapacitor's capability is shown in the formula below:

$$E = \frac{1}{2} CV^2 \quad (1)$$

in which C represents the capacitance. Given that the energy density, denoted by E , is directly proportional to capacitance, it becomes imperative to augment the capacitance to the greatest extent possible in order to maximize energy density and thereby efficiency. A practical method to enhance capacitance is by increasing the electrodes' surface area. The expansive flat layer inherent in the structure of graphene aligns perfectly with this prerequisite. There are mainly three types of supercapacitors: pseudocapacitors, hybrid capacitors and electric double-layer capacitors (EDLCs), in which graphene is mostly used in the last type. EDLCs are energy storage devices that store energy by means of a static charge as opposed to an electrochemical reaction that occurs in batteries. Figure 2 shows a simplified structure of cells with EDLC and pseudocapacitance [5].

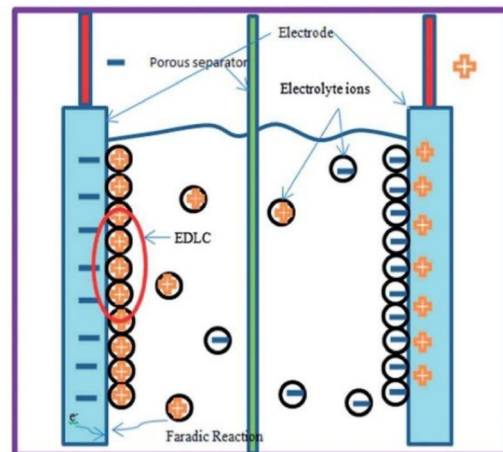


Fig. 2. Schematic showing 2-cell electrode configuration with both EDLC and pseudocapacitance from Tan et al. [5]

In an EDLC, the two electrodes are generally made of a highly porous material, such as activated carbon, which provides a large surface area for storing charge. These electrodes are often coated with a thin layer of a conductive material, which graphene is used for, to improve their electrical conductivity. Applying a voltage across the electrodes, ions from the electrolyte migrate towards the electrodes. Positive ions move towards the negatively charged cathode while the negative ions move towards the positively charged anode. This movement of ions creates a "double layer" of charge at the interface between the electrode and the electrolyte, hence the name "Electric Double-Layer Capacitor".

Charge storage in this double layer is facilitated through a process known as adsorption, wherein ions from the electrolyte attach themselves to the surface of the electrode. The quantity of charge that can be stored is contingent upon the surface area of the electrode and the characteristics of the electrolyte. This explains why materials possessing a large surface area, such as activated carbon or graphene, are employed for the electrodes. When the voltage is removed, the ions desorb from the electrode surface and return to the electrolyte, releasing the stored energy. The ability of the EDLC to quickly adsorb and desorb ions allows it to charge and discharge much faster than batteries, which rely on slower chemical reactions to store and release energy.

2.2 The role of graphene in supercapacitors

Graphene is a suitable material for the electrode covering due to its unique physical and chemical properties:

1. **High Specific Surface Area:** One of the most important properties of an electrode material in a supercapacitor is its surface area—the larger the surface area, the more charge it can store. Graphene, being a two-dimensional material, has an extremely high surface area (theoretically around 2630 m²/g). This characteristic enables the accumulation of a substantial quantity of charge within the double layer situated at the interface between the electrode and the electrolyte.

2. **Excellent Electrical Conductivity:** The rate at which a supercapacitor can charge and discharge is

directly related to the electrical conductivity of the electrode material. Graphene, with its sp^2 hybridized carbon atoms forming a planar structure, has excellent electrical conductivity. This is because the π electrons in the carbon atoms are delocalized over the entire sheet, allowing for easy movement of charge across the graphene layer.

3. Chemical Stability: Graphene is chemically stable and has a high tolerance for a wide range of temperatures. This makes graphene-based supercapacitors durable and suitable for a wide range of applications.

4. Flexibility and Mechanical Strength: Graphene is also known for its exceptional mechanical strength and flexibility, which can be beneficial in the fabrication and durability of supercapacitors.

Apart from those, the most important characteristic that despite graphene from other good conductors is its high porosity when in the form of graphene foam. The honeycomb-like pores present in the graphene layer offer channels for the ions in the electrolyte to reach the surface of the graphene sheet. This aspect is especially crucial in supercapacitors, given that the charge is stored at the juncture between the electrode and the electrolyte. Without these pores, the ions would only be able to interact with the outer surface of the graphene sheet, limiting the amount of charge that can be stored. In addition, the size and shape of the pores in graphene can be tuned to optimize its electrochemical properties. Research has shown that smaller pores can lead to higher capacitance in certain types of supercapacitors. A peak in specific capacitance when the interlayer constriction size reaches the diameters of unsolvated ions (Such as TEA^+ ions for 0.68 nm) [6]. This supports the hypothesis that the loss of ion solvation shell and anomalous capacitance increase was linked to sub-nanometer pores, and high capacitances ($120 Fg^{-1}$ and $80 Fcm^{-3}$) were observed in organic electrolytes when applied to microporous carbons (<1.5 nm) [7].

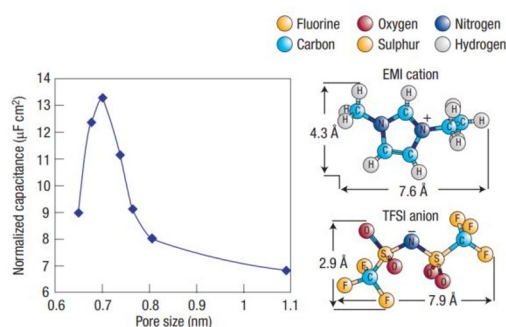


Fig. 3. Normalized capacitance change as a function of the pore size of carbon derived-carbide samples from Simon et al. [8]

Figure 3 shows the experimental result by preparing samples in EMI (ethyl-methylimidazolium) and TFSI (trifluoro-methane-sulphonylimide) at 60 °C in an ionic solution [8]. The peak capacitance is achieved when the size of the pore aligns with the maximum dimension of the ion.

2.3 Applications

Graphene-based supercapacitors are very potential for industrial applications. They can deliver large amounts of power quickly and be charged and discharged in very short periods, making them ideal for applications like regenerative braking in vehicles. They also have a long cycle life, withstanding massive amounts of charge and discharge cycles with minimal degradation. Additionally, their flexibility opens up possibilities for use in wearable technology and other applications requiring flexible form factors. For its strength in energy storage, a typical field where graphene-based supercapacitors are very potential to get industrialized production is the electric vehicle (EV) industry.

Skeleton Technologies, an energy storage enterprise based in Estonia, has entered into a collaboration with the Karlsruhe Institute of Technology (KIT), located in Germany, with the objective of creating a 'SuperBattery' designed specifically for electric vehicles. This innovative battery employs a hybrid system that amalgamates lithium-ion cells with the unique ultracapacitor cells developed by Skeleton Technologies. These ultracapacitors are fabricated using a material known as Curved Graphene. While the energy density of the SuperBattery does not suffice to entirely supplant lithium-ion batteries, it holds the potential to supplement the primary battery in fully electric vehicles during high-demand scenarios, such as during acceleration [9].

Shenzhen Toomen New Energy, a notable player in the industry, has developed a supercapacitor dubbed the Power Capacitor. This device matches the energy density of lithium batteries, a feat accomplished through a hybrid design that merges a lithium-ion battery with a traditional carbon-based supercapacitor, including a variant of graphene in one of the electrodes. The production of Power Capacitor cells is already in progress, and the participating companies are eagerly awaiting financial support to ramp up manufacturing [9].

However, it is crucial to recognize that these technologies are still under development and not yet widely implemented in commercial electric vehicles. The research is promising, but there are still challenges on energy density, scale of production, etc.

3. Use of graphene in gas sensors

3.1 Mechanism of graphene-based gas sensors

In addition to energy storage, the extraordinary electrical conductivity of graphene has also been used in sensing techniques. A study by Schedin et al. demonstrated that graphene-based sensors could detect individual gas molecules adsorbed on the graphene surface, leading to significant changes in the material's electrical resistance [10]. This sensitivity, coupled with graphene's robustness and flexibility, opens up new possibilities for the development of high-performance, low-cost, and compact gas sensors. Graphene-based sensors have a wide variety in different areas, such as biosensors, pH sensors, strain and pressure sensors, gas sensors, etc. The gas sensor is one of the most developed graphene-based

sensing techniques and has already been put in scaled industrial productions.

The mechanism of graphene-based gas sensors by utilizing the doping effect. When the pristine graphene is exposed to gases, gas molecules can either physically or chemically adsorb onto it. Physical adsorption (physisorption) includes weak temporary dipole forces, and chemical adsorption (chemisorption) involves the formation of chemical bonds. When a gas molecule adsorbs onto graphene, it can donate charge carriers (electrons) to or accept them from the graphene sheet. This transfer of charge carriers will influence the resistance of the graphene layer, by passing a current through the graphene sheet and measuring the voltage across it (or by using other electrical measurement techniques), one can detect the change in resistance caused by the adsorption of gas molecules. The magnitude and direction of the change can be indicative of the type and concentration of the gas.

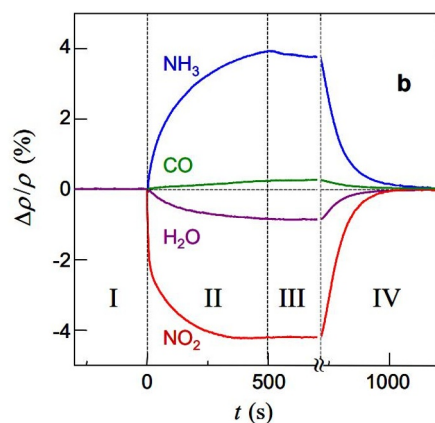


Fig. 4. Change of resistance of graphene after accessing in different gases from Schedin et al. [10]

Figure 4 shows the change of resistance (y-axis) against time (x-axis) after accessing ammonia, carbon monoxide, water vapour and nitrogen dioxide [10]. Among these, ammonia increases the resistance most while nitrogen dioxide reduces the resistance most. Hall measurements showed that ammonia and carbon monoxide are electron donors while water vapour and nitrogen dioxide are electron acceptors.

For electron donors, the lone electron pairs (on the nitrogen atom and oxygen atom respectively in this case) attack the positively charged carbon in the graphene layer, forming a single bond and donating the electrons into the graphene layer. Although the concentration of negative charge carriers in the layer increases, the additional electrons actually serve to scatter and hinder the mobility of the original charge carriers in the graphene. This scattering effect results in an increase in the electrical resistance of the graphene.

For electron acceptors, they tend to draw electrons away from the graphene sheet. It depletes the concentration of electrons in graphene. In intrinsic or n-doped graphene, where electrons are the majority charge carriers, this depletion of electrons effectively increases the concentration of holes (positive charge carriers). With the increased concentration of holes, the

mobility of these positive charge carriers is less hindered by the electrons. This is in contrast to the electron-donating gases which increase the electron concentration but scatter them, reducing their mobility. As the mobility and concentration of the positive charge carriers (holes) increase, the electrical resistance of graphene decreases.

As a result, graphene can be used to identify different types of gases under the same temperature and concentrations by observing the change in conductance caused by the doping effect. In addition, graphene can also be used to detect different concentrations of the same type of gas.

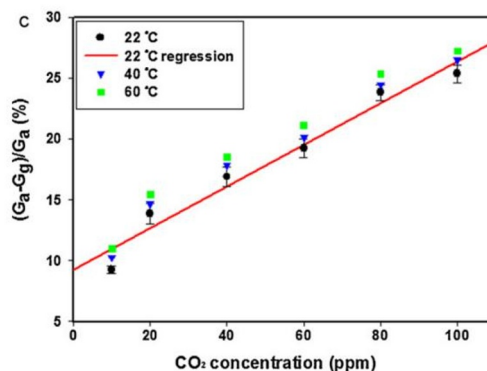


Fig. 5. Change of conductance of graphene under different concentrations of carbon dioxide from Yoon et al. [11]

Figure 5 shows the ratio of change in conduction (y-axis) to the change (x-axis) in the concentration of carbon dioxide in ppm [11]. The y-axis is calculated by the formula:

$$\Delta G\% = \frac{G_a - G_g}{G_a} \times 100\% \quad (2)$$

where G_a represents the conductance of graphene before accessing carbon dioxide and G_g represents the conductance after accessing carbon dioxide, so the difference in conductance divided by initial conductance turns out the percentage change of conductance caused by the carbon dioxide. As shown in the best-fit line, the conductance decreases as the concentration of carbon dioxide increases. This experiment was repeated three times but the error was less than 0.8%, which confirms that using graphene to detect and compare different concentrations of target gases is feasible.

3.2 Applications

Graphene-based gas sensors have garnered considerable attention in recent years due to their exceptional properties and promising applications across various fields. The practical uses of graphene-based gas sensors encompass the following subsections.

3.2.1 Environmental monitoring

Graphene-based gas sensors have exhibited high sensitivity and selectivity in detecting air pollutants such as nitrogen dioxide (NO₂), ozone (O₃), carbon monoxide (CO), and volatile organic compounds (VOCs). They offer the potential for continuous monitoring of air

quality in urban areas, industrial sites, and indoor environments.

Figure 6 shows an example of a graphene-based gas sensor for CO₂ and the obtained results are shown in Figure 5, proving its sensitivity [11]. Also, the curve in Figure 5 is generally linear throughout all concentrations of carbon dioxide, which indicates its high limit and wide range of detection. An infusion of 100 ppm carbon dioxide gas causes the conduction curve to peak at around 25% to 30% in 10 seconds, proving its selectivity and the short time required to respond.

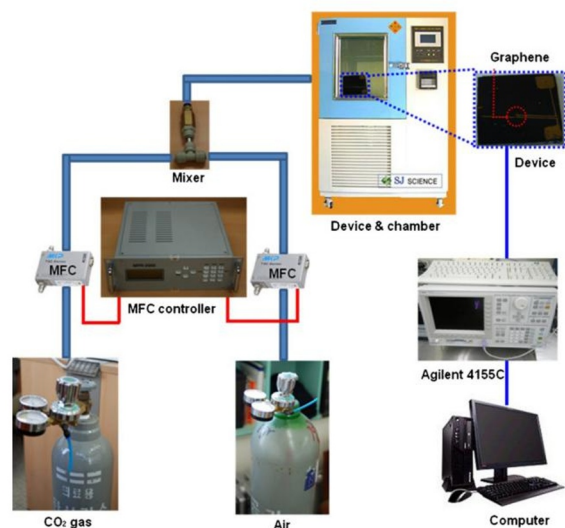


Fig. 6. An experimental setup for monitoring CO₂ presence and concentration using graphene from Yoon et al. [11]

3.2.2 Industrial safety

Graphene-based gas sensors hold promise in the detection of hazardous gases within industrial settings. They are capable of detecting gases such as hydrogen sulfide (H₂S), ammonia (NH₃), and methane (CH₄) even at low concentrations. As a result, they provide early warning systems to ensure worker safety in environments like mines, chemical plants, and oil refineries.

3.2.3 Healthcare and breath analysis

Graphene-based gas sensors have the potential to revolutionize healthcare through non-invasive breath analysis for disease diagnosis and monitoring. They can detect biomarkers present in exhaled breath, offering opportunities for early detection of diseases such as lung cancer, diabetes, and asthma.

These examples provide a glimpse into the diverse applications of graphene-based gas sensors. Ongoing research and development in this field continue to unlock new possibilities for addressing critical challenges in environmental monitoring, industrial safety, healthcare, food quality, and environmental protection.

4. Conclusion

In conclusion, graphene has developed applications in a wide range of fields in the past decade, especially in energy storage and sensing industries.

For energy storage, graphene is potential for its extraordinary conductivity, robustness and surface area for its application in supercapacitors. However, they face challenges including the expensive and complex production of high-quality graphene (which is also for the graphene-based gas sensors), a potential decrease in energy storage at high discharge rates, and difficulties in integrating them into existing technology due to their unique properties. Future directions for graphene-based supercapacitors include improving the cost-effectiveness and scalability of production, enhancing energy storage capacity, optimizing performance at high discharge rates, and developing strategies for seamless integration into existing technologies and infrastructure.

For its use in gas sensing techniques, graphene is suitable for a wide range of gas detection, having high sensitivity. It also has a high surface-to-volume ratio, allowing for a large sensing area. Challenges include issues with selectivity, as the sensors may respond to multiple types of gases, making it difficult to identify a specific gas in a mixture. Apart from more scalable productions, future directions of graphene-based gas sensors are mostly focused on improving their selectivity.

Despite the unresolved challenges, the significant potential of this technology has already been recognized by academics and researchers who continue to devote efforts towards its development. It is reasonable to maintain a strong conviction that, in the imminent future, this technology could serve as a pivotal tool to substantially enhance energy storage performance, and potentially instigate a revolution in the entire energy industry.

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