

Graphene Oxide – Cu Nanocomposites based on Reduced Graphene Oxide for Supercapacitor Applications

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Abstract - The study and use of extremely tiny scale structures and materials is known as nanotechnology. Subnanometer to several hundred nanometer ranges are common for typical measurements. A nanometer has a measurement of 10⁹ m, or one billionth of a meter (nm). Ten hydrogen atoms or five silicon atoms aligned together would not be much longer than a nanometer. Nanotechnology is more than simply a continuation of miniaturization from the micron to the nanoscale scale, which allows for greater functionality in the same amount of area. Micrometer-sized materials often share bulk materials' physical attributes, whereas nanometer-sized materials may have physical traits that are distinct from bulk materials. The modern electrochemical energy storage device, the supercapacitor, has several advantageous properties, including high power density, quick charge rates, long-life cycle stability, high specific capacitance, and low cost. Nanostructured materials, such as metals, metal oxides, and graphene nanosheets, have been increasingly employed in recent years for energy storage. Electrode materials based on 2-Dimensional reduced graphene oxide have several desirable properties for use in supercapacitor electrodes, including large surface area, remarkable electrical conductivity, good chemical stability, and excellent mechanical behavior.

Keywords - graphene oxide – Cu, nanocomposites, reduced graphene oxide, supercapacitor, applications.

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INTRODUCTION

The study and use of extremely tiny scale structures and materials is known as nanotechnology. Subnanometer to several hundred nanometer ranges are common for typical measurements. A nanometer has a measurement of 10⁹ m, or one billionth of a meter (nm). Ten hydrogen atoms or five silicon atoms aligned together would not be much longer than a nanometer. Nanotechnology is more than simply a continuation of miniaturization from the micron to the nanoscale scale, which allows for greater functionality in the same amount of area. Micrometer-sized materials often share bulk materials' physical attributes, whereas nanometer-sized materials may have physical traits that are distinct from bulk materials (Chua, 2014). Materials in this size range exhibit a number of interesting characteristics, including the transition from atoms or molecules to bulk form. At now, there are a wide variety of definitions floating around the internet on what nanotechnology actually is. A few examples of what nanotechnology entails include the creation and characterization of thin films and the use of electron microscopy to examine the microscopic structures of materials. Others think of nanotechnology as a bottom-up approach to materials

synthesis and manufacture which includes self-assembly or biomineralization to create hierarchical structures like abalone shells (Dhibar, 2017).

Microelectromechanical systems (MEMS) and lab-on-a-chip are two examples of nanotechnology. Drug delivery systems based on nanotechnology include encapsulating medication inside carbon nanotubes. Some people's ideas of what nanotechnology will look like in the future are rather fantastical and outlandish, such tiny submarines floating through the bloodstream, highly advanced self-replicating nanorobots keeping watch over our bodies, nanotube-based space elevators, and even space colonization. Professionals in the field of nanotechnology use several different umbrella terms to characterize their specialty. While any of these definitions may be appropriate in some contexts, they fail to cover nanotechnology as a whole. Nanotechnology is defined in a variety of ways since it involves so many diverse areas of research and calls for genuine transdisciplinary and interdisciplinary approaches. The term "nanotechnology" is often used to refer to the study, creation, and utilization of nanoscale components and systems. Nanotechnology also includes

research into the underlying physics of nanomaterials and nanostructures. Studying the fundamental connections between macroscopic physical properties and events and tiny material dimensions is what nanoscience is all about (Ciszewski, 2015).

In the United States, nanotechnology is defined as the study and use of materials and systems whose structures and components exhibit novel and significantly increased physical, chemical, and biological features, phenomena, and processes due to their nanoscale size. Exploring novel physical features and phenomena and realizing future applications of nanostructures and nanomaterials hinge on the ability to manufacture and process nanoparticles and nanostructures. Materials with at least one dimension in the nanometer range are included in the category of nanostructured materials. This includes thin films, nanorods and nanowires, nanoparticles, and bulk materials (Ejigu, 2018).

Energy storage device

In order to meet the energy demands of today's highly modern society, it's necessary to use and store energy on a massive scale, which calls for the integration of both distributed and centralized infrastructures. The need for faster and more beneficial energy storage systems has led to extensive research into advanced functional materials in recent years. Directly, as negative and positive electric charges on the plates of a capacitor in an electrostatic manner, a technique termed nonelectrical energy storage; and energy in batteries as chemical energy that requires Faradaic oxidation and reduction of electrochemically active chemicals to release charges that can perform electrical work when they flow between two electrodes with different electrode potentials. Although there have been tremendous efforts to develop high-performance Li-ion batteries and fuel cells, their limited power output and high maintenance costs have kept them out of many applications. Supercapacitors are becoming more popular as an alternative to conventional batteries and fuel cells due to their quick charge discharge rate, long lifespan, high power density, and absence of short circuit concerns. Supercapacitors are a kind of energy storage device that fill the gap between dielectric capacitors (which have a high power density but a low energy density) and batteries (which have a high energy density but also a large footprint). The surface area of the electrode, its electrical and ionic conductivity, its mechanical and chemical stability, etc. all have a role in the electrode's capacity to provide a large rate capability, a high specific capacitance, and a long life cycle in a supercapacitor (Nandi, 2020).

For this reason, several different electrode designs have been successfully produced and fine-tuned to make full use of the active materials and provide a high-performance supercapacitor electrode. The electrode materials for supercapacitors made of metals and metal oxides (M/MOs) have received a lot of attention due to their low cost, wide range of

oxidation states, high theoretical specific capacitance, and low environmental impact. However, nanoscale M/MOs can have electrode designs ranging from zero-dimensional (0D) to three-dimensional (3D) nanostructures; these designs can be effectively fabricated using methods like sol-gel methods, electrodeposition, electrospinning, and hydrothermal, allowing for their full utilization as electrode materials and the realization of a high-performance supercapacitor electrode. Graphene, a two-dimensional (2D) material with extraordinary thermal, mechanical, optical, and electrical properties, has attracted a lot of attention in recent years. Carbon atoms in graphene are sp² hybridized, and the carbon-carbon bond length in a single sheet of graphene is 1.42 angstroms. Carbon nanotubes (CNTs) or carbon nanorods (also called 0D carbon balls) and 1D carbon nanotubes (CNTs) or carbon nanorods (also called 3D graphite) encase the structure. Being a pure 2D substance that has never existed in nature before, graphene possesses several peculiar features (Maaoui, 2017).

Graphene, a two-dimensional (2D) version of graphite, is an example of a zero-bandgap semiconductor with very different characteristics from those of graphite in its 3D form. Also, its mobility is much higher than 15000 cm² /Vs at ambient temperature. Its electrical resistivity is theoretically lower than the gold and silver that are now used in industry standards (10⁻⁶.cm). In addition to its exceptional electrical characteristics, graphene also has an ultrahigh thermal conductivity of 4.85.3103 W/mK, which is almost five times the value of highly ordered pyrolytic graphite. On the other hand, graphene is the material with the highest tensile strength, at up to 130 GPa, as well as the highest spring constant, at 15 N/m, and the highest Young's modulus, at 0.5 TPa. Specific surface area is another crucial feature (SSA). Graphene, which consists of single sheets of carbon atoms, has great promise for catalytic and energy storage applications due to its very large surface area of 2675 m² /g. A few examples of electrochemical energy storage systems include fuel cells, batteries, solar cells, and supercapacitors. Hydrogen is the primary fuel for fuel cells, although it is a secondary energy source and can't be found in the environment. The high price of hydrogen energy stems from the difficulty of not only producing hydrogen from renewable sources, but also storing it (Wang, 2016).

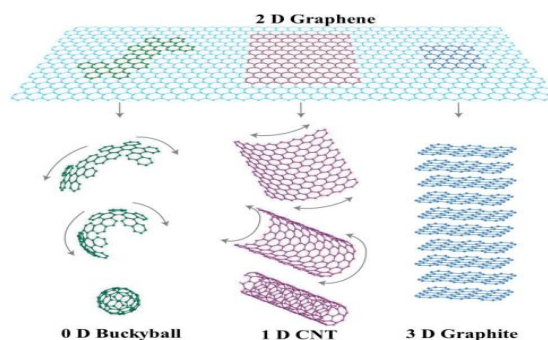


Figure 1: carbon allotropes with different dimensions

Capacitors

In the early days of electrotechnology, there were three main types of energy storage devices: (1) inductors, which relied on a magnetostatic field to hold energy; (2) batteries, which relied on chemical processes to hold energy; and (3) capacitors, which employed an electrostatic field. It is common knowledge that capacitors are one of the fundamental components of all electrical circuits. To store electrostatic energy, you may use a capacitor, which is a passive device with two electric terminals and no moving parts. Capacitors come in a wide variety of shapes and sizes, but they always have the same basic structure: two electric conductor plates separated by a dielectric. Capacitors come in a wide variety of shapes and sizes, but they always have the same basic structure: two electric conductor plates separated by a dielectric. Capacitors may be made from a wide range of materials, including metal thin sheets, aluminum foil, and disks. Capacitors' ability to store electrical energy is improved by a dielectric, which is itself nonconductive. While capacitors have been around for 200 years, the technology behind modern capacitors has only been around for 50 years (Jaikumar, 2015).

During the last fifty years, several technologies have been invented for the creation of improved capacitors. In contrast to their power, capacitors' limited energy storage capacity limits their usefulness. Electrostatic capacitors, which are the most common kind of capacitor, include two conducting electrodes separated by an insulator called a dielectric. An electric field is produced when charges accumulate on the two electrodes separated by an insulating dielectric layer and an external voltage is supplied. The gadget is able to store energy by virtue of the generated electric field.

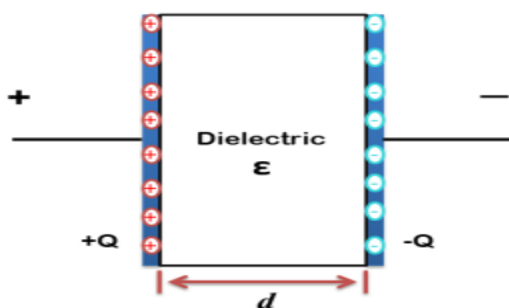


Figure 2: Electrostatic capacitor

Principle of Conventional Capacitor

The standard capacitor has two metal plates, or electrodes, and an insulating dielectric substance, or separator, between them. When voltage is applied, positive and negative charges congregate at the

electrodes. While doing so, the dielectric separator is employed.

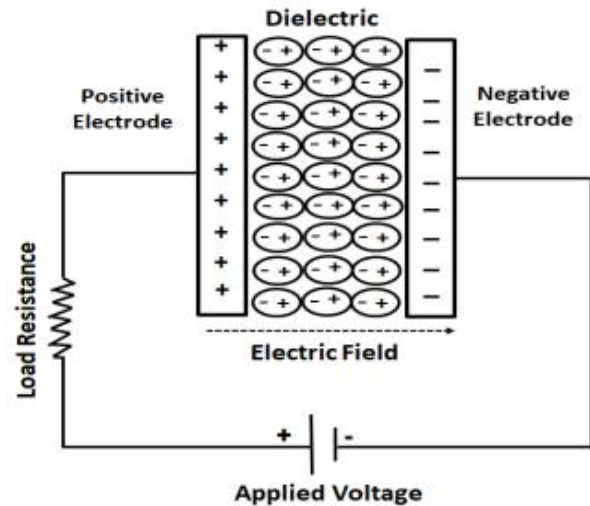


Figure 3: Conventional capacitor

Graphite

Graphite is one of the most common carbon allotropes and got its name from the Greek meaning "to draw" or "to write," "graphein," by Abraham Gottlob Werner in 1789. Unlike diamond, graphite is a good conductor of electricity. Hence, it may be used, for instance, as an electrode in electrical arc lighting. Graphite has been recognized as a mineral for over 500 years and has several practical applications including pencil lead and dry lubricants. Due to its strong in-plane thermal conductivity and low electrical resistance, it is a promising candidate for electrode material. Graphite is the most stable form of carbon under normal conditions. Thus, it serves as the standard for thermochemistry's definition of the heat required to produce compounds containing carbon. Graphite's ability to conduct electricity is due to the delocalization of the pi bond electrons above and below the planes of the carbon atoms. Since these electrons are unbound, electricity may flow through them (Purushothaman, 2014).

Nevertheless, electricity can only travel in a straight line between the layers. The four outer electrons of each carbon atom in a diamond are 'localized' between atoms during covalent bonding. Due to the low mobility of electrons in diamond, electricity cannot be transmitted through it. Graphite is made up of a network of covalent connections between carbon atoms, with each carbon atom sharing three of its four outer energy level electrons with two other carbon atoms in a plane. The chemical bonding process also involves a delocalized electron system, with each carbon atom contributing one electron to the system. Delocalized electrons may move freely in all directions on the sheet. Thus, electricity flows through graphite in a route parallel to the carbon

atoms' planes but not in a direction perpendicular to the plane.

Supercapacitors

Supercapacitors have come to the forefront as a viable energy storage alternative in light of the shortcomings of traditional battery and fuel cell technologies. Conversion equipment, such as supercapacitors, is a new kind of energy-saving technology with the desirable properties of high power density, rapid discharge charge, good circulation aspect, absence of self-discharging, safe operation, and cheap cost. Because to their extensive electrochemical properties, supercapacitors are often constructed using porous materials like MOs, carbon-based composites of M/MOs, and other composites like graphene-based M/MOs. regular form factor for a supercapacitor. Similar to the sandwiched architecture of capacitors, supercapacitors consist of two very porous electrodes. These two electrodes are immersed in an electrolyte and separated by a dielectric membrane through which ions may flow. When subjected to an external electric field, the device's two electrodes attract and collect opposite charges, or positive and negative ions, respectively. Electrolyte ions diffuse through the separator and into the electrode pores in accordance with the natural attraction rule of opposing charges (Shao, 2016).

Principle of supercapacitor

A supercapacitor is based on the same basic idea as a regular capacitor. Supercapacitors, like regular capacitors, have two electrodes separated by an insulating dielectric. The large surface areas of electrode material in supercapacitors, in comparison to normal capacitors, and an electrolyte solution are the primary differentiating factors between the two kinds of devices. When the surface area of a supercapacitor expands and the distance between its electrodes decreases, the device's capacitance and energy density skyrocket.

Carbon and allotropes:

Carbon's valency makes it capable of forming several different allotropes, or structurally diverse forms of the same element. Diamond and graphite are two common types of carbon. Sheet forms like graphene and ball forms like buckminsterfullerene are only two of the many allotropes that have been discovered and studied in recent decades. The nanoribbon, nanobud, and nanotube are all larger carbon structures. Among carbon-based materials, graphene and CNTs were the subject of much research because of the devices they enable, which store charges through non-Faradaic processes and rely on their conductivity and enormous surface area. By tailoring their structure and dimensions, they may be used for hydrogen storage, fuel cells, batteries, and supercapacitors. Several different types of carbon have been researched for their possible use in supercapacitors.

Carbon Nanotubes (CNTs):

The unusual properties of carbon nanotubes (CNTs), also known as buckytubes, make them an intriguing contender for a wide range of applications, including optics, nanoelectronics, and energy storage. They're strong, heat efficiently carry electricity, and have other amazing qualities. Nanotubes are a member of the fullerene structural family, along with buckyballs. In contrast to the spherical shape of buckyballs, nanotubes are cylindrical in shape, with at least one end often being capped with a hemisphere of the buckyball structure. Despite being several centimeters in length, nanotubes have a diameter on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair). CNTs are the most widely used building blocks in nanotechnology because of their beneficial physiochemical features (Bulin, 2016).

There are two main varieties of nanotubes, the single-walled (SWNT) and multi-walled (MWNT) types (MWNTs). For their nanoscale width (1 nm), SWCNTs are produced from single-layer graphene sheets wrapped around a central hollow core, whereas MWCNTs are built from two or more graphene layers wrapped together in a similar fashion. Nanotubes are formed entirely of sp² hybridized carbons, in contrast to the sp³ hybridization seen in diamonds. Extensive descriptions of their use may be found in the literature for sectors such as catalysis, waste-water treatment, biomedical applications, and energy conversion and storage devices.

Mesoporous carbon:

The International Union of Pure and Applied Chemistry defines mesoporous materials as those with pore diameters between 2 and 50 nm because of the remarkable properties they exhibit, including large specific surface areas, enormous pore volumes, programmable pore sizes, and controllable geometries. Mesoporous materials are promising candidates for these purposes because of their enhanced reactant transport efficiency and expanded active reaction sites. Due to the use of various precision manipulations and structural engineering approaches, effective mesoporous electrodes with excellent electrochemical performance have been established. Mesoporous materials have several applications in high-performance electrochemical energy storage devices, such as supercapacitors and rechargeable batteries. High-performance EDLCs have found renewed interest in ordered mesoporous carbons (OMCs) having highly ordered porous architectures. The initial report of the synthesis of highly OMC using the nanocasting process led to the development of a new class of OMCs with very high specific surface areas and pore diameters that can be tuned between 2 and 50 nm.

Graphene, Graphene oxide (GO) and Reduced Graphene Oxide (rGO)

Graphene, an allotrope of elemental carbon, was discovered in 2004; it is the first 2D crystal and has a sp²-bonded honeycomb arrangement. The simple yet successful technique of exfoliating a single layer of HOPG (highly oriented pyrolytic graphite) using common scotch tape was developed by physicist Sir Andre Konstantin Geim and physicist Sir Konstantin Sergeevich Novoselov. Since its discovery, this allotrope has quickly surpassed CNTs and activated carbons as the preferred electrode material for supercapacitors and captivated an entire scientific and technological province due to its extraordinary properties such as high specific surface area, anomalous quantum Hall effect, high thermal conductivity, outstanding mechanical strength, high optical transmittance, high young modulus, etc. In 2010, the Nobel Prize in Physics was awarded for the discovery of this extraordinary substance. This has led some to argue that graphene is the precursor of all graphitic materials, including buckyballs, CNTs, and graphite.

Properties of Graphene

Graphene has been dubbed a "wonder material" because to its exceptional physical and chemical features, and it has several applications across many fields. Graphene's strong conductivity, for instance, makes it a desirable material in electronics, where it also demonstrates chemical resistance, exceptional optical clarity, and mechanical stability. Being a single-layer, foldable material with a theoretical surface area of 2630 m² g⁻¹, it is an excellent alternative to indium tin oxide (ITO) for use in solar cell fabrication and energy storage devices. As compared to graphite (10 m² g⁻¹) and SWCNTs (1315 m² g⁻¹) as electrode materials, graphene stands out and garners a lot of interest. Graphene has been extensively reported as an electrode material in supercapacitor technologies, lithium-ion batteries, and fuel cells.

When a large quantity of the material is needed, chemical methods are favored for the synthesis of bulk chemically reduced graphene oxide (rGO) over the production of individual graphene layers. Just its use in supercapacitors will be discussed in this thesis. The capacity to insert oxygenated groups on both the basal and edge planes through covalent and non-covalent functionalization is perhaps the most important trait of graphene after considering its physical and chemical qualities. Covalent functionalization may alter the functionality of a material by attaching to preexisting functional groups in the material's basal plane. These preexisting functional groups include hydroxyl, epoxy, and carboxylic acid groups. They have both positive and negative effects on the heterogeneous electron transfer rate, which is an important aspect of the material's electrochemical properties. Furthermore, the attachment of various groups to the surface of GO and rGO by surface functionalizations of graphene

changes its electrochemical behavior. Nevertheless, noncovalent fictionalization uses weak -, electrostatic, and Vander Waals forces present in target molecules such polymers and other conjugated systems to bond to those molecules (Zhai, 2012).

CONCLUSION

There will soon be a supercapacitor device on the market with the same energy density as the existing lithium-ion battery. This energy storage system is so superior that it will usher in a technological revolution. In addition to the economic component and high performance of the electrode materials, achieving the stability factor in the electrochemical process is crucial in supercapacitors. As a result, a wide variety of M/MO (M=Cu, Ru)/rGO nanocomposites may be produced and their electrical and electrochemical performance studied, leading to the design of more effective supercapacitor electrodes. Studies in optics and electricity were also conducted by measuring UV-Vis and I-V properties. Moreover, electrochemical characteristics of the produced samples were investigated using CV, GCD, and EIS measurements. The data presented in this thesis show how incorporating M/MOs nanoparticles into a nanocomposite of varying morphologies might improve its overall performance.

REFERENCES

1. Chua C.K. and Pumera, M., (2014). Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. *Chemical Society reviews*, 43: 291-312.
2. Ciszewski, M., Mianowski, A., Szatkowski, P., Nawrat, G., and Adamek, J. (2015). Reduced graphene oxide–bismuth oxide composite as electrode material for supercapacitors, *Ionics*, 21: 557–563.
3. Dhibar, S., Das, C.K. (2017) Silver nanoparticles decorated polypyrrole/graphene nanocomposite: a potential candidate for next-generation supercapacitor electrode material. *Journal of Applied Polymer Science*, 134: 44724.
4. Ejigu, A., Fujisawa, K., Spencer, B.F., Wang, B., Terrones, M., Kinloch, I.A., Dryfe, R.A.W. (2018). On the role of transition metal salts during electrochemical exfoliation of graphite: antioxidants or metal oxide decorators for energy storage applications. *Advanced Functional Materials*, 28: 1804357.
5. Jaikumar, A., Santhanam, K.S., Kandlikar, S.G., Raya, I., Raghupathi, P. (2015). Electrochemical deposition of copper on graphene with high heat transfer coefficient. *ECS Transactions*, 66: 55–64.
6. Jo, K., Lee, T., Choi, H.J., Park, J.H., Lee, D.J., Lee, D.W. and Kim, B.-S. (2011). Stable Aqueous Dispersion of Reduced Graphene Nanosheets via Non-Covalent

- Functionalization with Conducting Polymers and Application in Transparent Electrodes. *Langmuir*, 27: 2014–2018.
7. Ke, Q., and Wang, J. Graphene-Based Materials for Supercapacitor Electrodes – a Review (2016). *Journal of Materiomics*, 2: 37-54.
 8. Maaoui, H., Singh, S.K., Teodorescu, F., Coffinier, Y., Barras, A., Chtourou, R., Kurungot, S., Szunerits, S., and Boukherroub, R. (2017). Copper oxide supported on three-dimensional ammonia-doped porous reduced graphene oxide prepared through electrophoretic deposition for non-enzymatic glucose sensing. *Electrochimica Acta*, 224:346–354.
 9. Nandi, D., Mohan, V.B., Bhowmick, A.K. and Bhattacharyya, D. (2020). Metal/metal oxide decorated graphene synthesis and application as supercapacitor: a review. *Journal of Materials Science*, 55: 6375–6400.
 10. Purushothaman, K.K., Saravanakumar B., Babu I.M., Sethuramana, B. and Muralidharan, G. (2014). Nanostructured CuO/reduced graphene oxide composite for hybrid supercapacitors. *RSC Advances*, 4: 23485–23491.
 11. Shao, Y., El-Kady, M.F., Lin, C.W., Zhu, G., Marsh, K.L., Hwang, J.Y., Zhang, Q., Li, Y., Wang, H., Kaner, R.B. (2016). 3d Freeze-Casting of Cellular Graphene Films for Ultrahigh-Power-Density Supercapacitors. *Advanced Materials*, 28: 6719-6726.
 12. Wu, Q., Xu, Y., Yao, Z., Liu, A., and Shi, G. (2010). Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films. *ACS Nano*, 4: 1963-1970.
 13. Yu, H., Zhang, B., Bulin, C., Li, R., and Xing, R. (2016). High-Efficient Synthesis of Graphene Oxide Based on Improved Hummers Method. *Scientific Reports*, 6: 36143.
 14. Zhai, D., Li, B., Du, H., Gao, G., Gan, L., He, Y., Yang, Q., and Kang, F. (2012). The preparation of graphene decorated with manganese dioxide nanoparticles by electrostatic adsorption for use in supercapacitors. *Carbon*, 50: 5034–5043.

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