

REVIEW ARTICLE



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ADVANCE IN COMPOSITE MATERIALS- GRAPHENE AND ITS APPLICATIONS IN MODERN COMPOSITE WORLD

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ABSTRACT

Ever since the discovery and application of the composite materials have begun there has been tremendous research and development to procure a better and more advanced composite materials than the previous ones. This resulted in the development of wide range of composites for various applications in almost every field of product development. One such composite is carbon fiber composite materials known for its light weight and high stiffness and strength. The carbon fiber composites is now becoming a talk of the past due to the recent discovery of a material called graphene. This material is now considered to be utilized to create composite materials which will lead the composite materials into new era. Compared to steel, the graphene paper (GP) is six times lighter, five to six times lower density, two times harder with 10 times higher tensile strength, and 13 times higher bending rigidity. These exceptional properties have opened up new opportunities for the application of this material in the future devices and systems. This article aims to present an overview of the advancement of research in applications of graphene in composites in different areas.

Keywords: graphene, graphene paper (GP) composite materials, graphene oxides (GO), Titanium dioxide-graphene.

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INTRODUCTION

Graphene is pure carbon in the form of a very thin, nearly transparent sheet, one atom thick. It is remarkably strong for its very low weight, it is 100 times stronger than steel and it conducts heat and electricity with great efficiency. Technically, graphene is a crystalline allotrope of carbon with 2-dimensional properties. In graphene, carbon atoms are densely packed in a regular sp²-bonded atomic-scale hexagonal pattern. Graphene can be described as a one-atom thick layer of graphite. It is the basic structural element of other allotropes, including

graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons.

Their thermal conductivity and mechanical stiffness rival the remarkable in-plane values for graphite (~3,000 W m⁻¹ K⁻¹ and 1,060 GPa, respectively); and recent studies have shown that individual graphene sheets have extraordinary electronic transport properties. One possible route to harnessing these properties for applications would be to incorporate graphene sheets in a composite material. The latest developments in larger scale production of graphene and its derivatives, in particular solution processing, have brought about their successful integration with polymers.

Using graphene in composite materials enhances the conductivity and strength of bulk materials, and can make use of graphene produced by less expensive methods like graphite exfoliation. These non-synthetic graphene are of insufficient quality to be used in most electronics applications, but they are perfect for use in Nanocomposites.

1.1 Electronic Properties-One of the most useful properties of graphene is that it is a zero-overlap semimetal (with both holes and electrons as charge carriers) with very high electrical conductivity. Carbon atoms have a total of 6 electrons; 2 in the inner shell and 4 in the outer shell. The 4 outer shell electrons in an individual carbon atom are available for chemical bonding, but in graphene, each atom is connected to 3 other carbon atoms on the two dimensional plane, leaving 1 electron freely available in the third dimension for electronic conduction. These highly-mobile electrons are called pi (π) electrons and are located above and below the graphene sheet. These pi orbitals overlap and help to enhance the carbon to carbon bonds in graphene. Fundamentally, the electronic properties of graphene are dictated by the bonding and anti-bonding (the valance and conduction bands) of these pi orbitals.

1.2 Mechanical Strength-Another of graphene's stand-out properties is its inherent strength. Due to the strength of its 0.142 nm-long carbon bonds, graphene is the strongest material ever discovered, with an ultimate tensile strength of 130,000,000,000 Pascals (or 130 gigapascals), compared to 400,000,000 for A36 structural steel, or 375,700,000 for Aramid (Kevlar). Not only is graphene extraordinarily strong, it is also very light at 0.77 milligrams per square metre (for comparison purposes, 1 square metre of paper is roughly 1000 times heavier). Graphene also contains elastic properties, being able to retain its initial size after strain. The graphene sheets (with thicknesses of between 2 and 8 nm) had spring constants in the region of 1-5 N/m and a Young's modulus (different to that of three-dimensional graphite) of 0.5 TPa.

1.3 Optical Properties-Graphene's ability to absorb a rather large 2.3% of white light is also a unique and interesting property, especially considering that it is only 1 atom thick. This is due to its aforementioned electronic properties; the electrons acting like massless charge carriers with very high mobility.

2. GRAPHENE COMPOSITE MATERIALS.

2.1 Silicon -Graphene Composites

A silicon-graphene Nanocomposites material for lithium battery anodes was developed by experimentation in order to achieve increase in energy capacity of battery. Graphite is the current standard material for this application, as it has a very high theoretical charge capacity. However, this large capacity is not practically accessible, as the lithium ions physically prevent from penetrating deep enough into the graphitic sheets. The research was conducted and a nanometer-sized defects were added into the graphene, to allow charge to flow more easily between layers, and added silicon nanoparticles in the 20-50 nm range between the sheets graphene - this resulted in up to a threefold increase in the energy capacity of the battery.

2.2 Titanium-Graphene Composites

Titanium is a major structural material for commercial, military and industrial applications, due to its corrosion resistance, high strength and light weight. However, its applications are restricted in many fields due to its low thermal conductivity. After intense studies by adding graphene to titanium significantly improved its thermal properties. The mass production of graphene nanoplatelets with the low-temperature metal processing technologies have begun after the development of titanium-graphene composites. In a further development it

was discovered that the presence of titanium made the hydrogen molecules bind to the graphene much more easily - suggesting potential applications for this type of material as a high-capacity hydrogen storage medium.

2.3 Graphene- poly (dimethylsiloxane) composite

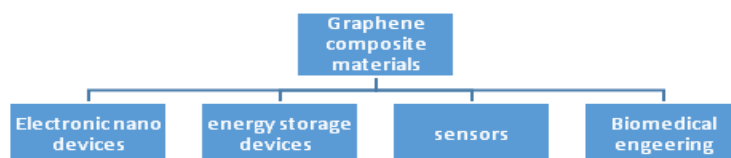
A new graphene-based polymer composite was developed and was found to be an excellent conductor of electricity. The material consists of a flexible, interconnected network of graphene embedded in a poly (dimethylsiloxane) matrix. The graphene foam was produced by depositing carbon onto a nickel foam template. Poly (methylmethacrylate) was then deposited on top of the thin carbon layer to prevent deformation of the structure. Treatment with a strong acid removed the nickel substrate, and the graphene foam was impregnated with poly(dimethylsiloxane) to create a light, flexible and highly conductive graphene-polymer composite.

2.4 Titanium dioxide-graphene (TiO₂-G) composite

A titanium dioxide-graphene (TiO₂-G) composite was developed and is used in the photo degradation of dangerous organic compounds in wastewater samples. The composite TiO₂-G was prepared using calcination and sonochemical methods. It was found that the synthesized TiO₂-G composites had enhanced photocatalytic efficiencies when compared to pristine TiO₂. Graphene provides a large surface area support for the TiO₂ photo catalyst and stabilizes charge separation by capturing electrons transferred from the TiO₂, thus hindering charge transfer and enhancing photocatalytic efficiency.

3. APPLICATION OF GRAPHENE COMPOSITES IN VARIOUS FIELDS.

Similarly there are various fields in which the graphene composite materials would help to improve the performance of the existing devices or systems tremendously. Some of the fields where the graphene composite materials are just discovered is shown below.



3.1 Electronic nano devices

➤ *Transparent conductive films* -With high electrical conductivity, high carrier mobility and moderately high optical transmittance in the visible range of spectrum, graphene composite materials show promise for transparent conductive films (TCFs) and is expected to be one of the mostly sought material for future optoelectronic devices [4, 6, 7]. Graphene TCFs have been used as electrodes for dye- sensitized solar cells, liquid crystal devices (LCDs) and organic light emitting diodes (OLEDs) [8, 9]. The high hole transport mobility, large surface area and inertness against oxygen makes graphene composites a promising candidate for photovoltaic applications. Graphene has been used as a novel acceptor for bulk heterojunction polymer photovoltaic cells, showing remarkably reduced photoluminescence and efficient energy transfer [5]. The high mobility and excellent mechanical properties of transparent graphene films makes it a suitable candidate for microelectronic applications. Kim et al. evaluated the fold ability of graphene films, transferred to a polyethylene terephthalate (PET) substrate coated with a thin PDMS layer by measuring resistance as a function of bending radii [4]. Liu et al. fabricated flexible graphene film on PET substrate from large size GO by thermal annealing and the green production of rGO films had potential application in flexible electronics [10].

3.2 Energy Storage Devices

➤ *Lithium Ion Battery*

Lithium ion battery has been a key component of hand-held devices due to its renewable and clean nature. To meet the increasing demand for lithium ion batteries with higher energy density and durability, new electrode materials with higher capacity and stability have been developed. Paek et al. has prepared graphene nanosheets decorated with SnO₂ nanoparticles. The SnO₂-Graphene exhibits reversible capacity of 810mAh/g and its cycling performance is drastically enhanced in comparison to that of bare SnO₂ nanoparticles [11]. Wang et al. have demonstrated self-assembled TiO₂-graphene hybrid nanostructure to enhance high rate performance of electrochemical active material [12].

➤ *Ultra capacitor.*

Chemically modified graphene (CMG) has been a potential material for the use as an electrode in ultra-capacitors [1, 13]. Graphene materials made by thermally expanding graphene oxide (GO) at high temperature [14] or alternatively at relatively low temperature (example 2000C) under vacuum (less than 1 Pa) [15] has been used as ultra-capacitor electrodes. There are several reports regarding graphene-based ultra-capacitors using metal oxides/ graphene [16-18], CNTs [19] and polymer/graphene composite [24, 20-22] as electrodes. Tang et al. prepared graphite oxide by modified Hummers method and the graphene thus obtained exhibited an enhanced storage capacity as an electrode material in super capacitors [23].

➤ *Fuel cell and solar cell*

Graphene composite materials have also been used in fuel cells and solar cells. Graphene has been identified as a catalyst support for oxygen reduction and methanol oxidation in case of a fuel cell configuration [25-29]. Conductive graphene scaffolds for platinum nanoparticles facilitates efficient collections and transfer of electrons to electrode surface. Graphene-based materials have been used as both window electrode and counter electrode in dye sensitized solar cells [6, 44]. Graphene doped conducting polymers such as poly (3, 4-ethylenedi-oxythiophene) poly (styrene sulphonate) (PEDOT: PSS) and poly (3- hexylthiophene) (P3HT) have shown better power consumption efficiency (4.5%) than cells with PEDOT: PSS as counter electrode (2.3%) [45]. Wang et al. demonstrated the influence of polymer/fullerene-graphene structure on organic polymer solar devices [46]. Hsu and his co- workers reported a layer-by-layer molecular doping process on graphene for forming sandwiched graphene/tetracyanoquinodimethane (TCNQ)/graphene stacked films for polymer solar cells [47]

3.3 SENSORS

➤ *Electrochemical Sensors*

Sundram et al. chemically modified graphene surface by electrodeposition of Pd nanoparticles. The electrodeposition of Pd on graphene improved the response of graphene sensors to H₂ detection [30].

Hu et al. prepared graphene nanosheets-gold Nanocomposites by microwave radiation which has got enhanced electrochemical response and can be used in highly sensitive electrochemical sensor [31].

Deng and his co-workers fabricated reduced graphene oxide (rGO)-conjugated Cu₂O nanowire mesocrystals for high performance NO₂ gas sensor [32].

➤ *Biosensors*

Wang et al. have designed an aptamer- carboxy fluorescein (FAM)/ graphene oxide nanosheets (GO-ns) nanocomplex to study the cellular target monitoring, which can be efficiently used for DNA and protein analysis and intercellular tracking etc. [33].

Yang et al. developed a label-free amperometric immunoassay for thrombomodulin using graphene/silver-silver oxide nanoparticles as a immobilization matrix [34].

Lian et al. developed a high sensitive uric acid sensor by using graphene doped chitosan as functional matrix and uric acid as template molecule and electrode position technique was used to form a controllable graphene-chitosan-uric acid composited film on glassy carbon electrode whose uric acid was removed via electrochemical induce elution [35]

➤ *Bio medical applications*

. The synergetic future of graphene composites and biotechnology holds great promise for its applications in the fields like gene and drug delivery, Tissue engineering and cancer therapy.

4. a. Gene delivery: Gene therapy is a powerful tool for the treatment of various diseases, both inborn and acquired by producing bioactive agents or stopping abnormal functions of the cells such as genetic disorder or uncontrollable proliferation of cells.

One of the key issues in this area is to develop nonviral gene delivery vectors or carriers with high efficiency of gene transfection, in which cationic polymers are usually involved [36-38]. Liu et al. and Chen et al observed that polyethylenimine (PEI) generally used during transfection when grafted to other system decreases the transfection efficiency, but PEI modified graphene oxide proved to be a promising candidate for efficient gene delivery [39-41].

Kim et al. developed a GO based efficient hybrid gene delivery carrier through the installation of low molecular weight branched polyethylenimine (BPEI) a cationic polymer, which has been widely used as an efficient non-viral gene delivery vector [42]

➤ Drug Delivery

In recent years, there has been a surge of interest in developing graphene for drug loading and delivery because of the strong interactions existing between hydrophobic drugs and aromatic regions of the graphene sheets. Liu et al. functionalized nano graphene oxide (NGO) a novel graphitic material with branched polyethyleneglycol (PEG) to obtain a NGO-PEG conjugate and use them for attaching hydrophobic aromatic molecules like camptothecin (CPT) analogue, SN38 noncovalently via $\pi-\pi$ stacking [2, 3]. A controlled loading of two anti-cancer drugs, DOX and camptothecin (CPT), onto folic acid conjugated NGO (FA-NGO) via $\pi-\pi$ stacking and hydrophobic interaction was studied by Zhang's group [43].

4. CONCLUSION

Graphene is a cheap and multifunctional material with unique physical and chemical properties. In addition graphene is an excellent electrode material for electroanalysis and electrocatalysis, and there is still much room for the scientific research and application development of graphene-based theory, composite materials, and devices. As well as the GS nanocomposites could be promisingly applied in many fields such as nanoelectronics, ultracapacitors, sensors, nanocomposites, batteries and gas storage. However, in spite of the considerable advances, substantial fundamental research is still necessary to provide a basic understanding of these materials to enable full exploitation of their nanoengineering potential. Graphene-based nanomaterials these days have led to an explosive growth of the research works on their biomedical applications can be observed from the literature in the past few years, especially in the areas of biosensors, bioelectronics etc. There is still much to be done for the scientific research and technological development of graphene-composite materials, and its applications in various fields.

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