A Route Towards Nano-Graphene Morphology and its Electrical Properties (A Review)

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Abstract - Graphene is a rapidly rising star on the horizon of materials science and condensed matter physics. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality, since the discovery of graphene, many efforts have been done to modify the graphene structure for integrating this novel material to nanoelectrical and electronic, energy storage devices and in many other applications. Graphene, an atomically has attracted tremendous attention in the scientific community due to its unique properties. Therefore, we have reviewed in detail the current developments of graphene based material with nanotechnology, its morphology to understand the importance and its applications. Specifically, much attention has been given to their wide range of electrical application in various fields, including electrochemical fields.

Keywords: Graphene, Nanotechnology, Electrical, Morphology.

I. INTRODUCTION

Nanotechnology is an emerging and dynamic field. Analysts argue that it is likely to have a horizontal impact across an entire range of industries and great implications on human health, the environment, sustainability, and national security [1].

Nanoparticulate drug carriers have been introduced as an important topic of research at the interface of nanotechnology and biomedicine because of their capacity for efficient drug loading and targeting [2]. The incorporation of nanomaterials in drug delivery has become a rapidly growing field. Numerous nano structured materials and their properties and uses have been described in the literature [3].

Graphene, a two-dimensional (2D) sheet of sp^2- hybridized carbon atoms, initially as a theoretical model for many years, was employed for describe the properties of other carbon-based materials [4]. How- ever, in 2004, Geim and Novoselov experimentally produced graphene sheets by mechanical exfoliation of graphite [5], and the unique properties displayed by this material, immediately bring it onto the focus of scientific research [6]. grapheme also has attracted great interest in physics, chemistry, and material science because of the unique electronic [7], thermal [8], and mechanical properties [9] arising from its strictly 2D structure, and to its potential technical applications [10].

While graphene sheets have been known to be components of traditional carbon materials, such as graphite, or components of a ‘‘new’’ class of carbon materials, such as carbon nanotubes, the route leading to the preparation of single-layer planar graphene sheets of atomic thickness [11]. Such two-dimensional carbon sheets possess unique properties, namely ballistic conductivity, high elasticity, very high mechanical strength, high surface area, and rapid heterogeneous electron transfer [12].

Bilayer graphene is also an important material as shown in **Fig. 1** and has very unique electronic structure and transport properties [13]. Another direction is of nanopatterned graphene structures, most notably grapheme nanoribbons consisting of one-dimensional stripes of the honeycomb arrangement, which lead to band gap opening, edge functionalization, etc. Depending on the edge shape, two important nanoribbons are armchair graphene nanoribbons and zigzag graphene nanoribbons shown in **Fig. 1.** Finally, when multiple graphene layers are stacked, one obtains graphitic materials, and multiple nanoribbons stacking leads to multilayer graphene nanoribbons.

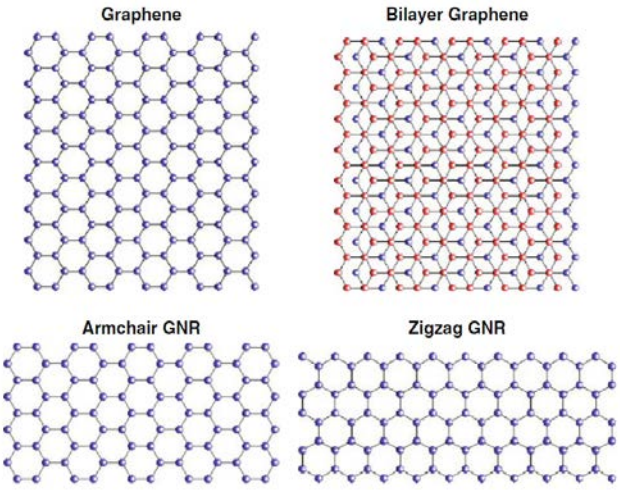


Fig. 1. Graphene and its nanostructures. Two graphene membranes with Bernal stacking order form bilayer graphene. One-dimensional nanoribbons with armchair

and zigzag edges conceptually extracted from the two-dimensional graphene are shown.

The use of nanomaterials in health and life-science applications has been steadily growing [14]. Graphene is considered the archetypal nanostructure within the family of carbon nanoforms, among fullerenes, carbon nanotubes, nanohorns, graphene quantum dots and others. Graphene materials (GMs; a family of materials including pristine graphene sheets, few-layer graphene flakes, graphene oxide and many others) offer a range of unique, versatile and tunable properties that can be creatively used for biomedical purposes. Their lateral dimensions can be adjusted between nanometres and millimetres, and their thickness can be tuned from single to hundreds of monolayers (also modulating flexural rigidityGraphene also provides a platform for relativistic quantum research [15]. Its high mobility up to 2 × 10^5 $cm^2V^{-1}s^{-1}$ makes it a candidate material for electronic applications beyond the silicon age [16].

Brief History of Graphene:

Historically, the word *graphene* comes from the Greek word *graphein*, which means *to write* – one of the earliest uses of this material. In the 1800s, the name *graphite* was given to the bulk material used in pencils by the German chemist Wagner. The most important historical application of graphite was in the molds to make cannon balls. It was truly a strategic material. The intercalation compounds of graphite were first reported in the 1840s and have been extensively studied since the 1930s [17]. In recent history, the use of graphite as a neutron moderator to thermalize high energy neutrons in nuclear reactors has been of great significance. The fundamental break throughs towards the physical understanding of graphene and graphite were routed in the 1940s and 1950s.

Modern derivatives also include carbon nanofibres (with diameters less than 10 nm) prepared and studied extensively in the 1970s and 1980s [18]. Graphene can also be conceptually thought of as a mother material for Bucky ball molecules and carbon nanotubes.

Before reviewing the earlier work on graphene, it is useful to define what 2D crystals are. Obviously, a single atomic plane is a 2D crystal, whereas 100 layers should be considered as a thin film of a 3D material. But how many layers are needed to make a 3D structure? For the case of graphene, the situation has recently become reasonably clear. It was shown that the electronic structure rapidly evolves with the number of layers, approaching the 3D limit of graphite already at 10 layers [19]. Moreover, only graphene and, to a good approximation, its bilayer have simple electronic spectra: they are both zero-gap semiconductors (can also be referred to as zero-overlap semimetals) with one type of electrons and one type of holes. For 3 and more layers,the spectra become increasingly complicated: Several charge carriers appear [20], and the conduction and valence bands start notably overlapping [20]. This allows one to distinguish between single-, double- and few- (3 to <10) layer graphene as three different types of 2D crystals ("graphenes"). Thicker structures should be considered, to all intents and purposes, as thin films of graphite. From the experimental point of view, such a definition is also sensible. The screening length in graphite is only ≈5Å (that is, less than 2 layers in thickness) and, hence, one must differentiate between the surface and the bulk even for films as thin as 5 layers [20].

Earlier attempts to isolate graphene concentrated on chemical exfoliation. To this end, bulk graphite was first intercalated [21], so that graphene planes became separated by layers of intervening atoms or molecules

There have also been a small number of attempts to grow graphene. The same approach as generally used for growth of carbon nanotubes so far allowed graphite films only thicker than ≈100 layers [22]. On the other hand, single- and few-layer graphene have been grown epitaxially by chemical vapour deposition of hydrocarbons on metal substrates and by thermal decomposition of SiC. Such films were studied by surface science techniques, and their quality and continuity remained unknown. Only lately, few-layer graphene obtained on SiC was characterized with respect to its electronic properties, revealing high-mobility charge carriers [23]. Epitaxial growth of graphene offers probably the only viable route towards electronic applications and, with so much at stake, a rapid progress in this direction is expected.

II. MORPHOLOGY

The graphene honeycomb lattice is composed of two equivalent sub-lattices of carbon atoms bonded together with sigma bonds, as shown in **Figure 2a.** Each carbon atom in the lattice has a ∏ orbital that contributes to a delocalized network of electrons. Whether freely suspended graphene has 'intrinsic' ripples or not has been addressed by Monte Carlo simulation [24] and transmission electron microscopy (TEM) studies [25]. The microscopic corrugations **(Figure 2b)** were estimated to have a lateral dimension of about 8 to 10 nm and a height displacement of about 0.7 to 1 nm. Sub-nanometer fluctuations in height forgraphene platelets deposited on an SiO 2 -on-Si substrate were studied by scanning tunneling microscopy (STM) [26] Although some STM experiments indicated a limited or negligible correlation between small (< 0.5 nm in height) corrugations and local electrical properties [27], evidence has been presented for strain induced local conductance modulations for bigger ripples (2–3 nm in height) [28]. Ripples can be induced [29], suggesting that the local electrical and optical properties of graphene could be altered through ‘ripple-engineering’ for possible application in devices.

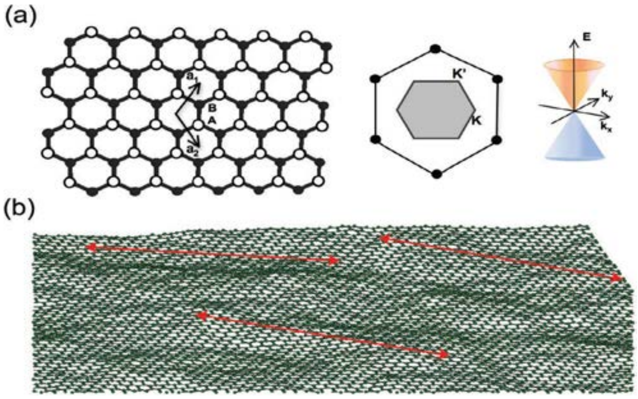


Figure 2 . (a) Schematics of the crystal structure, Brillouin zone and dispersion spectrum of graphene; (b) ‘Rippled graphene’ from a Monte Carlo simulation. The red arrows are 8 nm long.

Extrinsic morphology.

Recent studies reveal that, the *extrinsic* morphology of graphene on substrate surfaces or nanoscale scaffolds is *regulated*, distinct from the *random intrinsic* morphology of freestanding graphene. These studies on the extrinsic morphology of graphene illuminate new pathways toward fine tuning the corrugating physics, and thus the properties of graphene via external regulation. Teng Li etal reviews recent progress on modeling and experimental studies of the extrinsic morphology of graphene, aiming to offer a knowledge base for further research to explore these fertile opportunities in controlling graphene properties.

Many reviews the regulated extrinsic morphology of graphene on natural substrate surfaces and engineered substrate surfaces with one-dimensional (1D) and two dimensional (2D) patterned features, and then reviews the extrinsic morphology of grapheme regulated by zero-dimensional (0D) and 1D nanoscale scaffolds (e.g., nanowires and nanoparticles) patterned on a substrate. Concluding remarks are given in Section 4.

Extrinsic morphology of graphene on natural substrate surfaces

When fabricated on a substrate (e.g., SiO_2) via mechanical exfoliation or transfer printing, graphene also corrugates, which is often attributed to graphene’s intrinsic corrugations. However, recent experiments revealed that such random corrugations could be introduced by unwanted photoresist residue under the graphene if lithographic process is used. After careful removal of the resist residue, atomic-resolution images of the graphene on SiO_2 showed that the graphene corrugations result from its partial conformation to the SiO_2 substrate (**Fig. 3**) [30].

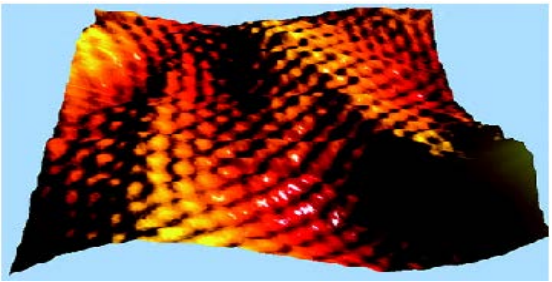


Fig. 3. Atomic resolution image of graphene partially conforming to a SiO2 substrate.

Energetics of extrinsic morphology of graphene under regulation

The extrinsic morphology of graphene regulated by the underlying substrate is governed by the interplay among three types of energies:

(1) graphene strain energy,

(2) graphene-substrate interaction energy, and

(3) substrate strain energy.

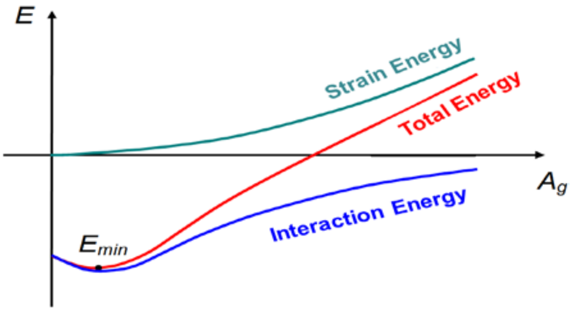


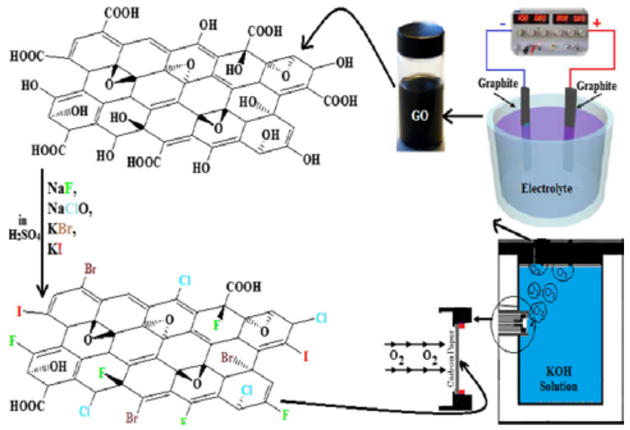
Fig. 4. Schematics of the energetics of the substrate regulation on graphene morphology. The strain energy and the graphene-substrate interaction energy are plotted as functions of the graphene corrugation amplitude $g\ A$. The total free energy minimizes at an equilibrium value of $g\ A$.

Teng Li etal , have reviewed some of the recent modeling and experimental investigations on the extrinsic morphology of graphene under a wide range of external regulation, ranging from 2D and 1D substrate surface features to 1D and 0D nanoscale scaffolds (e.g., nanowires and nanoparticles). It has been shown that the extrinsic morphology of graphene is governed by the interplay between the corrugation-induced strain energy in the graphene and the graphenesubstrate (and/or graphene-nanoscafolds) interaction energy.

III. APPLICATION OF GRAPHENE IN ELECTRICAL FIELD

1. Graphene as Electrocatalyst

Electro-catalysts for the oxygen reduction reaction (ORR) are key components of fuel cells (FCs). The FC, a device that converts chemical energy into electrical energy from a fuel through chemical reaction with oxygen, has drawn a lot of attention in terms of both fundamentals and applications [31].Halogen-doped reduced graphene oxide nanosheets as highly efficient metal-free electrocatalyst for oxygen reduction reaction, Karim Kakaei *etal* and Amin Balavandi *etal* demonstrate F-, Cl-, Br- and I-doped reduced graphene oxide (XRGO) as metal-free graphene electrocatalysts for oxygen reduction reaction (ORR) in alkaline media. Reduced graphene oxide (GO) is prepared from graphite electrode using electrochemical exfoliation. In situ doping of halide in a graphene film has many problems. In this technique, different halides individually or all of them were mixed with the RGO and ionic liquids precursor at H_2SO_4 solution. Then they have evaluated the effectiveness of doping and performed electrochemical measurements of 0 the ORR activity on XRGO. Fourier-transform infrared spectroscopy spectra show a variety of the halogen-containing functional groups. The electrochemical properties of the XRGO catalysts on carbon paper as a gas diffusion electrode (GDE) are investigated by several electrochemical methods in oxygen saturated alkaline solutions. The catalytic activity of the XRGO and Pt–C electrodes for ORR is 50 and 30 mA cm^{-2} at -1 V in GDEs. This enhanced efficiency is the result of the influence of the nature and percentage of the halogen, especially fluorine presence in the graphene layer.



Preparation of halogen-doped reduced graphene oxide (XRGO) nanosheets as highly efficient metal-free electrocatalyst for oxygen reduction reaction

Halogen-containing solutions were ready by adding 0.1 mol/L equivalent amount of KBr, KI, NaClO and NaF into 15 mL of H_2SO_4 10 mol/L in a glass bottle. In order to prepare of XRGO, 2.0 mg of RGO was added into the halogen-containing acid solution and dispersed by ultrasonic for 30 min. Then the solution was stirred at room conditions overnight. After filtration, the XRGO was washed with ethanol and water and finally dried at 40 ^{0}C to fabricate XIIRGO [32]. On the other hand, XIIRGO is a RGO nanosheets which doping by F, Cl, Br and I. Note that NaF has individually been introduced in the H_2SO_4 to produce FRGO and the other salts in the absence of NaF were mixed and XIRGO was obtained. XIRGO is formed of RGO doped by Cl, Br and I.

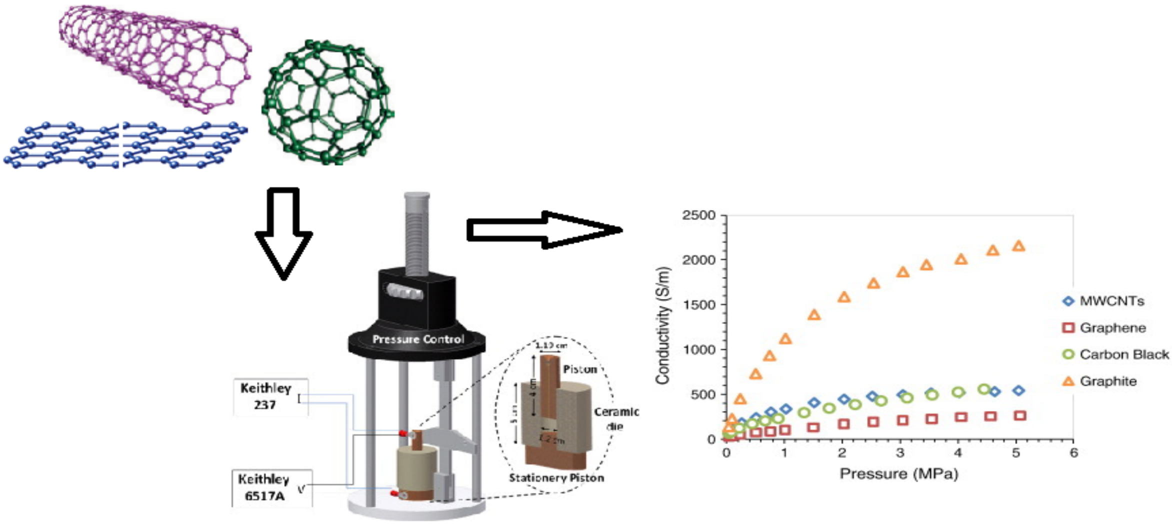
2. Electrical conductivity of compacts of graphene using powder compaction and paper formation, reflect their distinct morphologies.

Bernardo Marinho etal studied the electrical conductivity of different carbon materials (multi-walled carbon nanotubes, graphene, carbon black and graphite), widely used as fillers in polymeric matrices, using compacts produced by a paper preparation process and by powder compression. Powder pressing assays show that the bulk conductivity depends not only on the intrinsic material properties but is also strongly affected by the number of particle contacts and the packing density. Conductivities at high pressure (5 MPa) for the graphene, nanotube and carbon black show lower values (~ 10^2 S/m) as compared to graphite (~ 10^3 S/m). For nanotube, graphene and graphite particles, the conductive behavior during compaction is governed by mechanical particle arrangement/deformation mechanisms while for carbon black this behavior is mainly governed by the increasing particle contact area. The materials resulting from the paper preparation process for carbon black and graphite showed similar conductivity values as for the compacts, indicating a limited effect of the surfactant on the conductivity. The paper preparation process for the large surface area nanotube and graphene particles induces a highly preferred in-plane orientation, thereby yielding largely the single particle intrinsic conductivity for the in-plane direction, with values in the order of 10^3 S/m. [33]

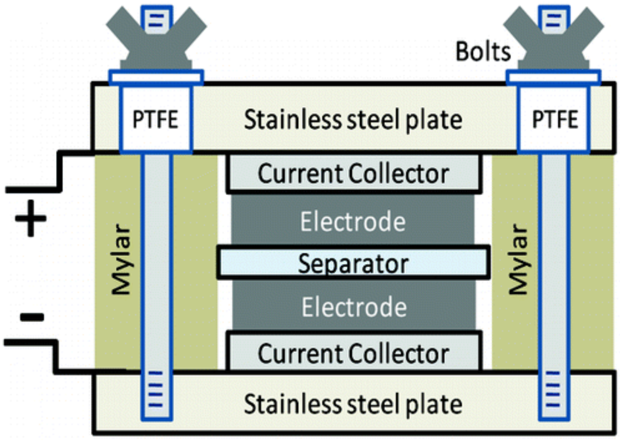
1. B Galindo etal synthesized graphene and few layers graphene were by a modified Hummers method using flake graphite powders as the starting material. The effect of the incorporation of graphene on the electrical properties of thermoplastic polyurethane (TPU). When solution blending is used for the preparation of composites, the obtained electrical conductivity is higher, even at very low loads (0,25% w/w). Moreover, the single layer graphene shows 10.000 times higher electrical conductivity than few layers graphene. [34]

2. To realize graphene-based electronics, various types of grapheme are required; thus, modulation of its electrical properties is of great importance. *Dacheng Wei etal* synthesize the N-doped graphene by a chemical vapour deposition (CVD) method. We find that most of them are few layer graphene, although single-layer graphene can be occasionally detected. As doping accompanies with the recombination of carbon atoms into graphene in the CVD process, N atoms can be substitutionally dopped into the graphene lattice,

which is hard to realize by other synthetic methods, electrical measurement show that the N-doped graphene exhibits an N-type behavior, indicating substitutional doping can effectively modulate the electrical properties of graphene. Our finding provides a new experimental instance of graphene and would promote the research and application of graphene. [35]



3. ZhihongChen etal have fabricated graphene nano-ribbon field-effect transistor devices and investigated their electrical properties as a function of ribbon width. Our experiments show that the resistivity of a ribbon increases as its width decreases, indicating the impact of edge states. Analysis of temperature-dependent measurements suggests a finite quantum confinement gap opening in narrow ribbons. The electrical current noise of the graphene ribbon devices at low frequency is found to be dominated by the 1/*f* noise [36].



4. Meryl D. Stoller etal synthesized a new carbon material that we call chemically modified graphene (CMG). CMG materials are made from 1-atom thick sheets of carbon, functionalized as needed, and here we demonstrate in an ultra capacitor cell their performance. Specific capacitances of 135 and 99 F/g in aqueous and organic electrolytes, respectively, have been measured. In addition, high electrical conductivity gives these materials consistently good performance over a wide range of voltage scan rates. These encouraging results illustrate the exciting potential for high performance, electrical energy storage devices based on this new class of carbon material [37].

5. Graphene as flexible electronics (Displays that bend)

Jong-Hyun Ahn etal and *Byung Hee Hong etal* discuss how graphene can be used in the development of flexible electronics. Electronic components that are flexible and stretchable are more versatile than rigid ones, and are sought after for optoelectronic devices such as displays, solar cells and light emitters. In optoelectronic devices, transparent electrodes are key components, and at present are typically made from indium tin oxide (ITO) because of its relatively good conductivity and optical transparency. But ITO has poor mechanical properties: when bent or stretched it tends to crack, and this leads to a deterioration of its electrical properties.

Graphene has emerged as a promising material for transparent and flexible electrodes. The optical transmittance of monolayer or few-layer graphene grown by chemical vapour deposition (CVD) is superior to that of ITO and other emerging materials, and the sheet resistance of graphene films is comparable to that of ITO because of graphene's high carrier mobility (>103 cm2 V^{-1} s^{-1}) and high carrier density (>1012 cm^{-2} for doped samples) .The use of graphene as a transparent electrode has already been demonstrated in a variety of flexible optoelectronic devices, including touch-screen sensors (Figure), organic light-emitting diodes and organic photovoltaic devices. The possibility of fabricating lightweight, thin and low-cost flexible electronics devices through continuous roll-to-roll processes is another important advantage of using graphene electrodes. Resolving the challenges will bring closer the advent of flexible electronics, in which graphene technology will be as stretchable as our imagination [38].

IV. ACKNOWLEDGEMENTS

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