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Chapter

Graphene Nanopores

Per A. Löthman

Abstract

Graphene is a two-dimensional, atomic thin, usually *impermeable* nanomaterial with astonishing electrical, magnetic and mechanical properties and can therefore at its own right be found in applications as sensors, energy storage or reinforcement in composite materials. By introducing *nanoscale pores* graphene alter and extend its properties beyond permeability. Graphene then resembles a nanoporous sensor, a nanoporous, atomic thin membrane which opens up for such varied applications such as water purification, industrial waste water treatment, mineral recovery, analytical chemistry separation, molecular size exclusion and supramolecular separations. Due to its nanoscopic size it can serve as nanofilters for ion separation even at ultralow nano- or picomolar concentrations. It is an obvious choice for DNA translocation, reading of the sequence of nucleotides in a DNA molecule, and other single molecular analyses as well for biomedical nanoscopic devices since dimensions of conventional membranes does not suffice in those applications. Even though graphene nanopores are known to be unstable against filling by carbon adatoms they can be stabilized by dangling bond bridging via impurity or foreign atoms resulting in a robust nanoporous material. Finally, graphene's already exceptional electronic properties, its charge carriers exhibit an unusual high mobility and ballistic transport even at 300 K, can be made even more favorable by the presence of nanopores; the semimetallic graphene turns into a semiconductor. In the pores, semiconductor bands with an energy gap of one electron volt coexist with localized states. This may enable applications such as nanoscopic transistors.

Keywords: graphene, carbon, DNA, bottom-up, translocation, sculpting

1. Introduction

Pores are *ubiquitous* in nature, engineering and the natural sciences. We recall such diverse examples such as porous light weight metals, aluminum foams or metallic hollow spheres structures [1–4] that can save energy by reduced gas consumption, or cell membranes with ion-channels which constitute highly functional nanoporous structures of the cell. They are responsible for maintaining the required pressure gradient, ion-flux and ultimately nutrition and life itself in both mono- and multicellular organisms. One of the simplest but highly ordered proteinaceous nanoporous membranes in nature are bacterial surface layers (s-layers), a spontaneously occurring protective layer on the surface of the bacterial cell. This regularly structured nanoporous membrane protects and regulates a minimum out- and influx of nutrients to the cell and can be used as templates to synthesize metallic nanoparticles in the lower nanorange (1,4 nm) or as a soft membrane in nanobio-devices [5]. Nanopores such as the protein hemolysin are found in cell membranes, acting as transport channels for ions or molecules in and out of cells [6–8]. The

selection mechanism of these membranes can be based on size exclusion as well as exclusion based on double layer overlap and dielectric exclusion [9]. S-layers are together with the cell membrane one of numerous *soft-matter* nanoporous materials. While cell membrane ion-channels or s-layers serve several life sustaining, protective biological functions they are not durable or mechanical stable and therefore not suitable for engineering applications. Quite the opposite are *solid state* nanopores which presents obvious advantages over their soft-matter counterparts. They are highly stable, exhibit controllable dimensional parameters such as channel length and diameter. Their surface characteristics can be altered and enable integration into devices and arrays.

A solid state material which has gained considerable recognition the last decade is *graphene* considered as one of the strongest and thinnest materials known. Monolayer Graphene possesses astonishing characteristics: Its electron mobility is 100 times higher than silicon; it conducts heat twice as good as diamond; its electrical conductivity is 13 times better than copper and it absorbs only 2.3% of reflecting light i.e. it is transparent; it is impenetrable even to the extent that the smallest atom (helium) cannot pass through a defect-free monolayer graphene sheet; and its high surface area of 2630 m^2/g which means that with less than 3 grams you could fully cover an entire soccer field. It is a two-dimensional atomic thin allotrope of carbon consisting of a single layer of atoms arranged in a two-dimensional hexagonal honeycomb structure [10, 11]. The name reflects the fact that the graphite allotrope of carbon consists of stacked graphene layers [12]. They are bound to each other by weak van der Waal forces which makes graphene an integral part of the 3D material graphite from which it was first isolated. Graphene was however not expected to exist in the free state i.e. as a single monoatomic layer. Scientists had argued convincingly that monoatomic thin 2D materials like graphene would be too thermodynamically unstable to exist. Thermal fluctuations would be as large as the force binding the atoms together, causing the structure to fall apart [10, 11]. However, carbon bonds are in fact strong enough and small enough that thermal fluctuations are not enough to destabilize graphene even at room temperature. Free-standing monolayer graphene was isolated in 2004 by Novoselov and Geim [13, 14] and follow-up investigations revealed several novel exciting properties [15, 16]. Graphene was considered as the new material of the future and Novoselov and Geim were awarded the Nobel Prize in Physics for their discovery and characterization of graphene.

Graphene has excellent *mechanical and electrical* properties: an atomic thin monolayer graphene has an inplane direction independent Young's modulus of 1 TPa and strength of 100 GPa [17–21].

Graphene's superior electrical properties are due to the fact that its charge carriers are massless Dirac fermions [10–12] with high mobility and ballistic transport even at highest electric-field and affected to only minor degree by chemical doping. Its extraordinary high electrical conductivity and its capacity to carry large currents at room temperature [22] makes it indeed an exciting material. Carbon atoms have four electrons available to make chemical bonds. Graphene is however only one atom thick and every atom in the crystal is bound to only three others. Each atom thus has one free electron available for electronic conduction which means that graphene by far exceed the electrical properties of metals. Since each graphene 2D lattice provides as many charge carriers as metals are only able to supply from bulk 3D atomic architectures, even when metals tend to have some electrons delocalized and shared in a "sea of electrons" among all atoms within a piece of metal, which makes graphene an extraordinary material in electronics [23]. In electronics graphene may act as scaffold on which parts that can act as distinct components may self-assemble into an electronic circuit. This is due to the fact that various molecules

can attach to the graphene surface due to its electronic structure and that chemical changes made to parts of the graphene sheet such that local electric properties can be fine-tuned and varied on the same surface along with additional properties such as permeability via nanopores (sculpting). Such nanometer-sized circuitry may one-day enable faster and smaller computational and electronic devices.

Moreover, the specific electrical properties of graphene in terms of conductivity are due to the fact that with one p_z electron per atom in the model the valence band is fully occupied, while the conduction band is vacant. The two bands touch at the zone corners (the K point in the Brillouin zone), where there is a zero density of states but *no band gap*. The graphene sheet thus displays a *semimetallic* (or *zero-gap-semiconductor*) character, although the same cannot be said of a graphene sheet rolled into a carbon nanotube, due to its curvature. By introducing nanopores in graphene one can open up an energy band gap in a graphene sheet as described below.

Conceptually graphene represents a new class of materials; inorganic, two-dimensional materials that are only one atom thin. Thereby graphene provides new incursions into low-dimensional physics which has always been a rich source for novel applications. Graphene does no longer requires any further proof of its importance in terms of fundamental physics, however, there is still room for extending, altering and improving graphene properties. As already mentioned *nanoscopic sculpting* such as nanolithography, manipulation by AFM [24] or an electron beam of a transmission electron microscope [25] is considered a promising venue to target properties of nanomaterials. In this way nanopores can be introduced into graphene. It has become an alternative route of materials development; instead of turning to a different class of graphene-based materials such as nanoribbons or nanocomposites, sculpting nanopores into graphene would further alter the already numerous and exceptional properties and extend the fields of applications. It would open up an energy band gap in a graphene sheet for the application as field effect transistors (FETs) [25–27]. Nanopores can turn *semimetallic* graphene into a *semiconductor* [28].

Nanoporous graphene exhibit a *periodic arrangement* with nanoscale diameters in the graphene membrane. Apart from Nano sculpting as mentioned above numerous methods, such as chemical etching [29], vapor deposition [30], and electron beam [31], have been developed to fabricate nanoporous materials and control pore dimensions. Moreover, it is expected that facile methods such as self-assembly of graphene are just as suitable for nanoporous graphene as it is for impermeable graphene or grapheneoxide [32–34].

The aim of this work is to illustrate how the properties and applications of the nanoscopic material graphene can be altered, improved and extended by introducing nanopores in the graphene layer.

2. Ion transport through graphene nanopores

Transport phenomena through ion exchange membranes have been investigated for several decades. When L. Michaelis first observed the effect of membrane charge on the ion transport through pores in the year 1926 [35, 36] there has been an continuous interest in this research field and the transport phenomena are now well understood for conventional dense ion exchange membranes. The current trend towards nanotechnology and miniaturization of devices, ion transport through solid state nanopores is gaining attention [37–41]. 2D materials such as graphene play an important role for applications in nanofluidic device, biosensing, and DNA translocation [42–45].

2D materials may have some limits in these applications because of the presence of intrinsic defects and low surface charge density. The ion selectivity may be influenced by the pore size distribution. These membranes exhibit low surface charge which limits rejection of ions. It is therefore important to optimize fabrication techniques combined with a thorough understanding of transport phenomena through a 2D interface. It is expected that transport under nano-confinement in 2D is expected to differ from highly charged ion exchange membranes.

A number of different physical transport processes occur in the pores of a membrane. The most relevant processes for ion transport and ion separation processes the most important are size exclusion, charge exclusion and dielectric exclusion [46]. Size exclusion occurs when the pore size of the membrane is comparable or smaller than the species to be retained.

Microfiltration (MF) membranes have relatively large pore sizes (0.1–10 μm), to separate smaller species from 1 to 100 nm (e.g. proteins, viruses), ultrafiltration (UF) membranes are used. Nanofiltration (NF) membranes (1–10 nm) are used for removal of salt, amino acid, and dye [47]. Dielectric exclusion is an ion rejection mechanism observed in NF membranes and typically dominates at <1 nm and effective up to about 2 nm pore size [46, 48]. This phenomena occurs at interfaces between media having different dielectric constants. The mutual interaction of ions at the surface and the induced bound electric charge at the interface leads to the dielectric exclusion. This also depends on pore geometry e.g. cylindrical pores have stronger exclusion compared to slit pores. Ion exchange membranes (IEM) are used for demineralization or deionization of water, energy conversion and energy storage in fuel cells, redox flow batteries [49, 50].

Other than these commercial membranes, nano-porous materials such as solid state nano-pores in synthetic membranes (SiN_x, SiO_2), *nano-porous graphene*, graphene oxide multi layers, metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and hybrid membranes can act as *ion selective membranes* depending on the ion concentration.

Konatham *et al.* studied water transport through monolayer graphene nanopores via molecular dynamics (MD) simulations. The pore diameter war as small as 7.5–14.5 Å in the monolayer graphene [51]. In this case ion exclusion was achieved up to a 7.5 Å pore diameter of non-functionalized (uncharged) pores. Larger pores cannot block the ions. Dielectric exclusion may also in this case be an important mechanism of exclusion for pore sizes close to 7.5 Å.

The ion rejection mechanism in pores is influenced by functionalized pores. Functionalization with carboxyl groups show improved ion rejection due to a higher free energy barrier towards water and ions. Because of this ion screening effect, the free energy barrier decreases with increasing salt concentrations in the bulk. Cohen-Tanugi *et al.* showed via MD simulation that multilayer *graphene membranes* can desalinate water more effectively than monolayer graphene. The salt rejection mechanism as a function of pore diameter, layer spacing and applied pressure was investigated. The smaller nanopores (3 Å) reject salt entirely compared to larger pores (4.5 Å) and highly aligned pores with multiple layers can even combine high salt rejection with high water flux [52].

Graphene pores supported on track etched PCTE membranes and pores were enlarged by oxidative etching in acidic potassium permanganate solution was investigated. The number of pores were 1012/cm^2 and the pore sizes were in the sub nanometer (0.40 ± 0.24 nm) range. For short oxidative etching times, the resulting membrane showed cation selective behavior because of steric exclusion and the negatively charged surface groups at the pores. A membrane potential around 4 mV was observed for 0.5 M KCl/0.1667 M KCl which is lower compared

to the theoretical Nernst potential for this salt concentration ratio (28.1 mV). This indicates that the pore sizes may be larger than 0.4 nm as the selectivity is expected to be higher at 0.5 M KCl due to dielectric exclusion. The membrane potential decreased with increase in pore size obtained after longer oxidative etching times.

Oxygen (O_2) plasma etching is an additional fabrication method to create graphene nanopores; CVD graphene transferred onto a SiN substrate with a 5 μm hole and subjected to O_2 plasma etching. This generates nanometer sized holes in the graphene sheet which was confirmed by Raman spectroscopy. Nanopores fabricated via this method have shown very high *salt retention* at lower etching time due to the small pore size. The transport properties of ions through these nanoporous interfaces were investigated with or without externally applied electric fields [53–60].

Nanoporous graphene is *cation selective* [61, 62] and a non-linear current–voltage relationship has been detected [63]. A diode rectification effect has widely been observed especially in solid state conical nanopores [54, 56]. For graphene nanopores and other 2D materials (MoS_2, h-BN) the rectification effects has been observed in both intrinsic and artificially made pores [61, 64–68]. Nanoporous graphene supported on PET shows an ion rectification effect due to the presence of *conical* nanopores as a result of *asymmetric etching* [64–68]. Applying an external potential and gating the graphene the ion selectivity can even be *tuned* [69].

Up to date most investigations were limited to sub-nanometer sized pores in graphene where the ion rejection was mainly dominated by steric exclusion.

The ion-selectivity of graphene nanopores favors K^+ over Cl^- even up to a pore diameter of 20 nm. The selectivity calculated by the Goldman-Hodgkin-Katz (GHK) model was around 100, a value much higher than the selectivity observed by Jain *et al.* for pore sizes of sub-nm level (0.4 nm) [63]. The membrane potential, specially for biological membranes is typically calculated using the GHK voltage Equation [70–76]. This equation is applicable for multiple permeating monovalent species and it takes into account the permeability of each specie. Furthermore, the selectivity was dependent on the pH. The cation to anion selectivity decreases with decreasing pH which was attributed to the protonation of surface charged groups e.g. carboxyl groups at the graphene edge. Interestingly, the membrane could differentiate between monovalent and divalent cations by conducting monovalent cations 5 times faster than divalent cations. Ion selective transport through graphene with pores larger than a nanometer was experimentally shown by Rollings and van Deursen et al. [74, 75].

Molecular dynamics simulations by Cohen-Tanugi *et al.* show that nanoporous free-standing graphene membranes are able to reject NaCl ions while letting water flow at permeabilities several orders of magnitude higher than conventional reverse osmosis membranes. The performance was studied as a function of pore size, chemical functionalization, and applied pressure. The results indicate that the membrane's ability to prevent the salt passage but allowing for water flow depends critically on pore diameter. Also chemical functional groups bonded to the edges of graphene pores suggests that commonly occurring hydroxyl groups can roughly double the water flux thanks to their hydrophilic character. Nanoporous graphene may play an important role for water purification. The maximum diameter for salt permeability is around 5.5 Å, that is, Na + and Cl- ions will pass through the membrane beyond this diameter [77].

Other molecular dynamics studies by Suk *et al.* found that pure water can continue to flow across graphene nanopores with diameters below 1 nm, and calculations suggest that the chemical functionalization of graphene nanopores could be tuned to selectively reject certain solvated ions [78–81].

3. Single molecule analysis via graphene nanopores

Nanopores resemble a class of a biosensor, allowing for highly sensitive detection of biomolecules including nucleic acids and proteins at single-molecule resolution [76, 82, 83]. Nanopore sensors have emerged as powerful devices for probing biomolecules and offer a novel platform for single molecule analysis and characterization. In particular, they have attracted significant attention as tools for high-throughput, robust, and low-error DNA sequencing. Especially graphene and other two dimensional (2D) materials are being investigated with respect to their integration into nanoscaled devices that may in the future sequence genomes. The successful implementation of solid-state nanopores in emerging third-generation DNA sequencing applications is contingent upon developing methods for scalable fabrication, high-accuracy output, and integration with low-noise electronic architectures.

In a nanopore ion currents and forces can be monitored as molecules pass through. This makes it possible to investigate a wide range of phenomena involving DNA, RNA and proteins. The solid-state nanopore increasingly proves to be a surprisingly versatile new single-molecule tool in biophysics and nanofluidics.

The high sensitivity of the nanopore comes from the characteristic structure of the nanopore: a nanometer scale pore as large as the size of the molecule of interest [84, 85]. It allows for detection of biomolecules even at a sub-nanomolar concentration level and discrimination of minute differences in molecular structure between different nucleotides [86–88]. The high sensitivity originates from the electric potential applied across the nanopore membrane which generates a highly concentrated electric field near the nanopore. Charged molecules pass through the narrow pore one molecule at a time [87].

The methods in use for biomolecule translocation detection include resistive pulse sensing [89–92], tunneling current detection [42, 93, 94] and optical sensing, [95–99]. In the resistive pulse technique (or Coulter-counter method), the nanopore acts as the only channel across the membrane for both ions and biomolecules, and partial blocking of the nanopore by a biomolecule is directly reflected in a perturbation in the measured ionic current. More precisely, a membrane containing a single nanopore is sandwiched between two reservoirs of electrolytic solution, such as aqueous potassium chloride. Ions are driven through the pore, as illustrated in **Figure 1**, by applying an electric potential difference across the membrane, resulting in an ionic current that can be measured. When the electrolyte contains larger charged molecules, such as DNA or proteins, these are also driven through the pore, causing a transient dip in the ionic current where each current dip represents a passage, or translocation, of a biomolecule, with the magnitude and duration of the pulse being indicative of the molecule's radius and length, respectively.

Moreover, slowing down the DNA translocation speed has been a major issue for nanopore sensing. The DNA translocation speed is a few orders of magnitude faster in the solid-state nanopore than in a biological nanopore for unknown reasons [95].

To slow down translocation speed in the solid-state nanopore, various engineering strategies have been enivsaged: dragging the molecule by strengthened interaction with the modified or chemically decorated pore surface. Here materials including aluminum oxide (Al_2O_3)–graphene etc. integrated with the nanopores slows down the DNA translocation by an enhanced Coulombic, specific, or hydrophobic nonspecific interaction between the nanopore surface and DNA [101, 102].

Various research groups investigated the influence of the number of nanoporous graphene layers on the DNA translocation; 1 or 2 layers thick [103], 1–8 layers thick [101] and 3–15 layers thick [102]. Initial DNA detection experiments were carried out, an important step towards DNA sequencing. In each case the nanopores could

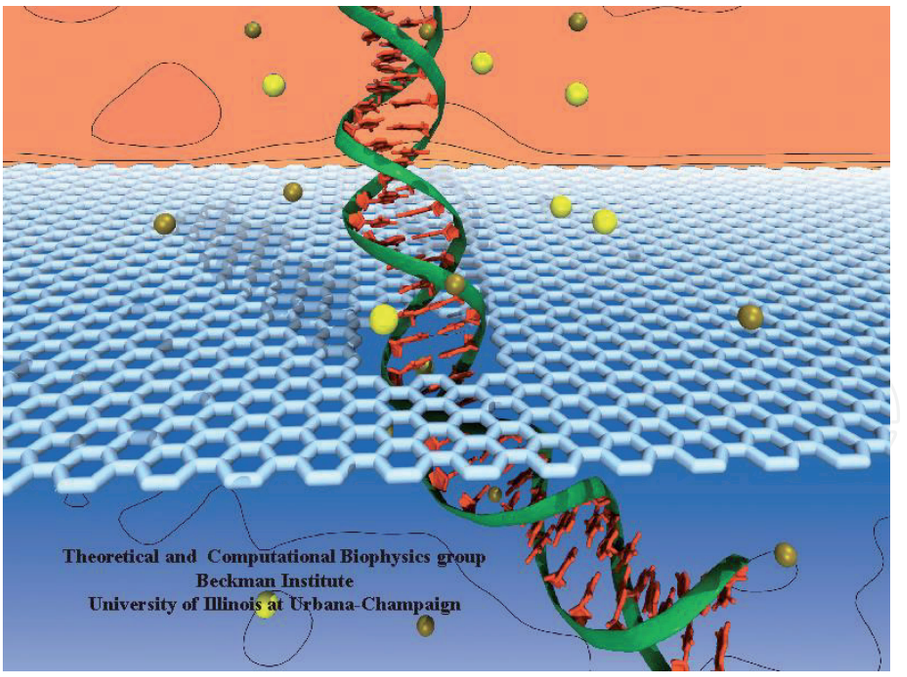

Figure 1.
A DNA molecule translocating through a graphene nanopore [100].

detect double stranded DNA molecules with lengths from 400 to 48,000 base pairs. Even membranes with significant variability in the baseline current levels were found to be viable for DNA detection. Interestingly the nanopores could differentiate between DNA that passed through the pore in an extended form and that which passed through in a folded form. Even though these developments are impressive, the central goal remains unsolved: is singlebase resolution with a graphene nanopore feasible? Also in this case all the different nanoporous graphene membranes did show that the translocation events are too fast to be resolved by the existing detection electronics.

4. Mechanical and electrical properties of nanoporous graphene

Nanoporous graphene is unique in that it exhibits both *electronic functionality* as a *tunable* semiconductor and *mechanical functionality* as a *tunable* molecular filter membrane. These properties combined in a single atomically-thin, mechanically robust platform makes nanoporous graphene a promising candidate for electronically active nanodevice applications [104–106].

As is noted, a better understanding of the structure–property relation would be of direct relevance to the structure design and function optimization in a variety of technological applications. The present study aims at the mechanical properties of nanoporous graphene membranes. Many attempts have been made to exploit the basic properties of nanoporous graphene membranes for functional applications. In this context Cohen-Tanugi *et al.* [105] used molecular dynamics simulations and continuum fracture mechanics in order to study the mechanical resilience of nanoporous graphene as a reverse osmosis membrane. The mechanical properties such as strength depend on the nanopore architecture in the nanoporous graphene materials and the nanopore diameter of the substrate .

An energy band can be opened by introducing nanopores in a graphene sheet for example for application as field effect transistors (FETs) [101, 102, 106]. Semimetallic graphene, the normal state of graphene, can turn into a semiconductor

by introducing nanopores . The opening and tuning of a bandgap in nanoporous graphene membranes and the dependence of electronic properties on the structural parameters has been investigated in theory [102, 103].

The energy bandgap of semiconducting graphene nanopores, a chirality dependent scaling rules have been suggested. On the basis of extensive tight binding studies and simple geometric arguments, *Lee et al.* report that Pedersen scaling governs not only the energy bandgap but also the effective mass of the Bloch electron of the semiconducting graphene nanopores regardless of its chirality or the crystallography of pores when the nanopore areal fraction is low [102].

To open a tunable bandgap in graphene, which is required for semiconductor materials, has been desirable for novel applications of graphene. One strategy of constructing periodic nanopores in graphene to form graphene antidot lattices (GALs) has been extensively studied The electronic structure of graphene antidot lattices with zigzag hole edges was studied with first-principles calculations. It was revealed that half of the possible GAL patterns were unintentionally missed in the usual construction models used in earlier studies. With the complete models, the bandgap of the GALs was sensitive to the width W of the wall between the neighboring holes. A nonzero bandgap was opened in hexagonal GALs with even W, while the bandgap remained closed in those with odd W. Similar alternating gap opening/closing with W was also demonstrated in rhombohedral GALs. Moreover, analytical solutions of single-walled GALs were derived based on a tight-binding model to determine the location of the Dirac points and the energy dispersion, which confirmed the unique effect in GALs [103].

Hu *et al.* [101] investigated the mechanical behavior and fracture mechanism of nanoporous graphene NPG for porosities up to 80% and marked the transition of mechanical behavior at a critical porosity of ~15%. Carpenter *et al.* [102] analyzed the dependence of elastic properties on the architecture of graphene nanopore arrays (the pore arrangement, pore morphology, material density, and pore edge passivation), and further established the scaling law between modulus and relative density. Moreover, Liu *et al.* [106] carried out MD simulations to study the mechanical properties of nanoporous graphene with the pore size ranging from 0.4 nm to 1.3 nm, and for the first time revealed the relationships between mechanical properties (Young's modulus and fracture strength) and porosity. These investigations have a shed light upon deformation behavior and mechanical properties of nanoporous graphene.

5. Fabrication of graphene nanopores

Graphene seems to be an ideal material to create nanopores because it is mechanically and chemically robust even when being atomically thin. A defect free graphene layer is completely impermeable. For this reason, pore creation is necessary to investigate transport mechanisms through graphene nanopores as well as altered mechanical and electronic properties. Pore creation in this two dimensional material is challenging as it is difficult to handle this monolayer graphene without creating additional defects and cracks.

The first attempts to fabricate nanoporous graphene was based on the *top-down approach* in which the structures were created via electronbeam lithography (nano sculpting) or directly etched from graphene, patterned by using self-assembled etch masks as described in the upper part of **Figure 2**. The top-down method do however not lead to small nanopores that can open band gaps of roughly 1 eV (comparable to that in silicon, a conventional semiconductor material). The diameter should be less than 2 nm to meet this requirement [27, 108] for implementation in devices. Since this is beyond the structural resolution of top-down approaches successful attempts

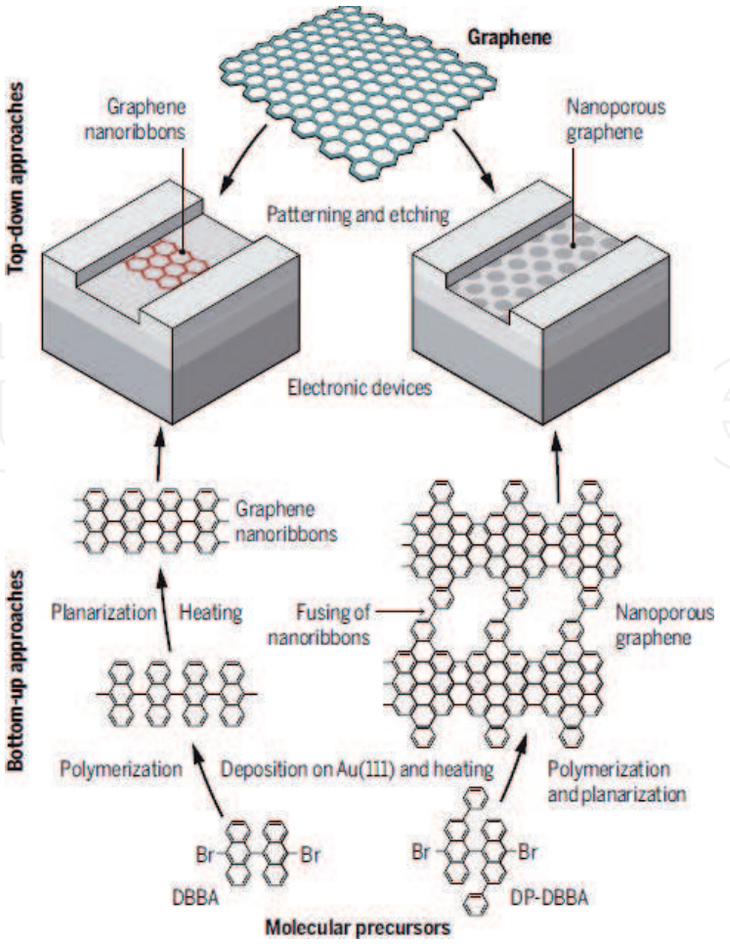

Figure 2.
Nanopores can be introduced in graphene by top-down or bottom-up strategies. Top-down approaches involve patterning and etching of graphene sheets. The resulting pore structure are often too large for device applications that require a band gap. Bottom-up assembly using molecular precursors can overcome this limitation as shown in the lower part [28, 107].

to create graphene nanopores of the desired size was rather achieved via *bottom-up* approaches (lower part of **Figure 2**). Starting from molecular building blocks, such as DBBA (10,109-dibromo-9,99-bianthracene) and other halogenated molecular precursors [28, 109] very narrow graphene nanoribbons could be made with atomic precision when sublimed onto a single crystal Au(111) substrate. The molecules form linear polymer chains in ultra-high vacuum (UHV) at about 200°C and annealing at 400°C where the chains planarize and fuse. Other halogenated polycyclic aromatic hydrocarbon precursors lead to a large variety of structurally different graphene nanoribbons via similar on-surface reactions [102] and of the nanoribbons are not entirely straight i.e. a non- uniform width, prior to fusion, they produce graphene nanostructures with nanoscopic holes after an extra annealing at 450°C which is the case when diphenyl-substituted DBBA (DP-DBBA) is sublimed on Au(111) substrate in UHV. Several spectroscopic studies have shown that the resulting nanoporous graphene has a highly anisotropic electronic structure with a band gap of about 1 eV [110].

Additional bottom-up strategies use polyphenylene units through surface-assisted coupling of halogenated molecular building blocks [108, 109] as well as chevron-shaped graphene nanoribbons fused to form nanoscale graphene nanopores [110]. Other bottom-up methods such as chemical etching [18], vapor deposition [25], and electron beam [26], have been developed to fabricate NPG materials and control the characteristic size. Moreover, it is even possible to realize a *single nanopore* in a graphene sheet as Rollings *et al.* have shown via fabricating a single nanopore supported on SiNx by an electrical pulse method [74].

Graphene nanopores are the material of choice for applications in nanodevices and in this context it should be mentioned that characterization where graphene are implemented is still a challenge. The short length scales (mostly around <50 nm) as well as the necessity of accurate alignment relative to the device structure, and high contact resistances, and in studies of electrical properties of nanoribbons the yield of working devices is often rather low. On the other hand nanoporous graphene could form larger electrically conducting domains, from which devices for electrical property measurements could be produced at yield as high as ~75% yield [110, 111].

6. Conclusion

It is obvious that for improvement and alteration of graphene properties introducing nanopores into the graphene sheets can open up novel fields of application for graphene. Nanoporous graphene design is of equal importance in terms of improving long-range order of nanopores, avoiding defects and establish accurate dimensional control and increasing yield. Here the bottom-up approach seem to have advantages over the top-down approach. Hopefully the potential of nanoporous graphene will stimulate chemists to develop new molecular precursors for nanoporous graphenes with various combinations of structural parameters (size, geometry and arrangement of pores). To induce periodic, atomically-precise nanopores and to tailor precise dimensions and electronic properties and to fabricate nanoporous graphene with complete atomic precision is a future goal. However the present highly anisotropic structure of nanoporous graphenes may also be of interest for spectroscopic studies. Graphene nanostructures with nanoscopic pores may be of interest for applications such as separation, sensing, and potentially even DNA sequencing. Since nanopores in graphene open up the band gap and makes the material semiconducting promising applications in mostly FETs but also water filtration, supercapacitors, biological analysis, DNA translocation and molecular sieving among others can be envisaged [112, 113]. It is because of the extended plethora of properties of nanoporous graphene that it is considered to be the next leap forward in carbon based nanomaterials research.

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