

Chapter 2

The Properties of Vertically-Oriented Graphene

Abstract The unique properties of vertically-oriented graphene (VG) are discussed in this chapter. VG is intrinsically graphene, but it also possesses unique structural features, i.e., being arranged perpendicularly to the substrate surface. Therefore, VG possesses not only the properties of graphene but also some unique characteristics induced by its oriented arrangement. We start this chapter with a brief introduction of some general properties of graphene, which is deemed reasonable and necessary before we elaborate on the uniqueness of VG. To illustrate the attractive characteristics of VG, we compare VG with planar (or horizontal) graphene structures and emphasize the benefits that can be brought about due to VG's vertical orientation. The unique properties of VG are summarized at the end of this chapter. Understanding of the VG's uniqueness is critical to appreciating why VG has attracted so much interest and is also an essential step toward tailoring VG properties for various applications.

Keywords Ballistic electron mobility • Hybridization • Plasma-enhanced chemical vapor deposition • Orientation • Specific surface area • Thermal conductivity • Vertically-oriented graphene

2.1 General Characteristics of Graphene

The past decade has seen a fast-growing interest in graphene. This strong interest in graphene was initiated by some groundbreaking works in the early 2000s [1–3] and has been further enhanced by the Nobel Prize in Physics in 2010 [4]. However, graphene research started long before 2004 [5]. For example, the theoretical work in 1947 by Wallace [6] predicted that graphene (or single crystal graphite with interactions between planes being neglected, as the term “graphene” was unavailable at

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that time) might have extraordinary electronic characteristics (e.g., 100 times greater conductivity within a plane than between planes). In 1986, the term “graphene” was recommended to name a single carbon layer of the graphitic structure [5, 7, 8].

Graphene possesses many extraordinary properties and has been the subject of intense scientific interest. Exceptional values have been reported of: ballistic electron mobility (theoretical limit: $\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [9]; experimentally measured to be $2.53 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [10]), high thermal conductivity (5000 W/m-K) [11], Young’s modulus ($\sim 1100 \text{ GPa}$), fracture strength (125 GPa) [12], a high specific surface area ($\sim 2630 \text{ m}^2/\text{g}$) [13], and optical absorption of exactly $\pi\alpha \approx 2.3 \%$ (in the infrared limit, where α is the fine structure constant) [14]. To comprehend these outstanding properties, one must first look at the unusual electronic structure of graphene.

Electronic properties. As the sixth element in the periodic table, carbon has a $1s^2 2s^2 2p^2$ ground state electron configuration (i.e., two electrons in the inner shell and four in the outer shell). For a carbon atom in graphene, the four valence orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$) are sp^2 hybridized (i.e., the mixing of the single $2s$ orbital with two $2p$ orbitals), resulting in three planar σ orbitals separated by 120° with each other and one remaining $2p$ orbital ($2p_z$) oriented perpendicular to the graphene plane. Each of the three sp^2 orbitals of a carbon atom forms a σ bond (0.142 nm in length) with three neighboring carbon atoms on the 2D plane, forming the hexagonal structure of graphene with a basis of two atoms (A and B) per unit cell (Fig. 2.1a) that has the in-plane lattice constant of $a = 0.246 \text{ nm}$ and the thickness of 0.335 nm. The carbon-carbon σ bonds are strong covalent bonds, which are responsible for the lattice stability and for the elastic properties of graphene. The adjacent interaction among neighboring $2p_z$ orbitals develops into delocalized π (bonding) and π^* (anti-bonding) bands, which form the valence band (VB) and the conduction band (CB), respectively (Fig. 2.1b).

The π and π^* bands of graphene are degenerate at the corner (K point, or Dirac point) of the hexagonal Brillouin zone. For low energies associated with electron transport, the bands have a linear dispersion and the band structure can be regarded as two cones touching at E_D (the so-called Dirac crossing energy) (Fig. 2.1c). Since the VB and the CB touch at E_D , graphene has a zero bandgap

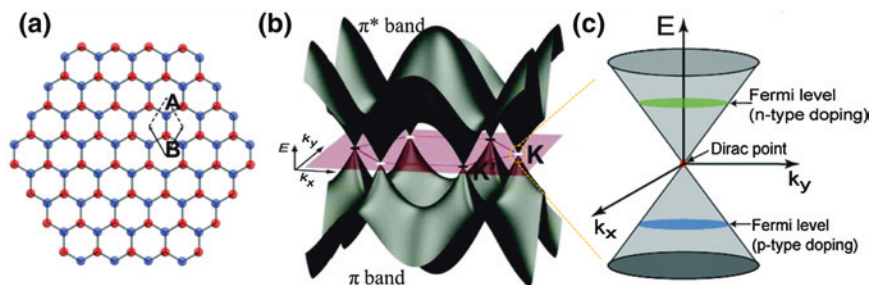


Fig. 2.1 **a** The hexagonal lattice of graphene has a basis of two carbon atoms (A, B) per unit cell. **b** The π and π^* bands in graphene. **c** The linear dispersion and the band structure at the Dirac point. Reprinted with permission from [16]. Copyright 2010 American Chemical Society

and is thus typically labeled as a zero-gap semiconductor, or a semimetal. The extraordinary electronic properties of graphene are a direct result of the unusual band structure of graphene, i.e., a zero bandgap with linearly dispersing bands that touch at the Dirac point. The charge carrier mobility in graphene is very high, with experimental results of $\sim 2.53 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [10] and theoretical prediction of $\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [9]. The charge carriers (electrons and holes) are able to travel a micrometer scale without scattering (known as ballistic transport) at room temperature [15]. Due to its atomic thickness, charge carrier transport through graphene is highly sensitive to adsorption/desorption of molecules, making graphene a promising material for both gas sensing and biosensing.

Mechanical properties. The covalent carbon-carbon bonds in graphene are very strong and nearly equivalent to the bonds holding carbon atoms together in diamond, giving graphene similar mechanical and thermal properties as diamond. Graphene is one of the strongest materials and has a Young's modulus of 1 TPa and an intrinsic strength of 130 GPa [12]. Since every atom in graphene is a surface atom, the specific surface area of graphene is extremely high and is theoretically predicted to be $2630 \text{ m}^2 \text{ g}^{-1}$. Graphene is also very light, with a density of 0.77 mg/m^2 ; it would only take about 4 g of graphene to cover an American football field ($110 \text{ m} \times 48.8 \text{ m}$).

2.2 Planar Graphene Versus Vertically-Oriented Graphene

The intrinsic properties of graphene can be unfavorably modulated when graphene sheets are laid down and in direct contact with a substrate. When graphene is laid on a substrate, the interaction between π electrons of graphene and the substrate electrons can considerably alter the electronic structure and lower the carrier mobility of graphene. For example, with SiO_2 as the substrate, the carrier mobility of graphene is limited to $\sim 4 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, which is much lower than the theoretical limit ($\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). In addition, interactions with the underlying substrate are largely responsible for the presence of strong impurity scattering in graphene, which restricts the electron mean free path to less than a micron [17, 18].

When graphene sheets are placed randomly on a substrate, they tend to form irreversible agglomerates or restack due to the strong π - π stacking and van der Waals interactions, demolishing the potentials that could be offered by individual graphene sheets. Although a graphene sheet has exceptional electrical conductivity along its basal plane, the out-of-plane conductivity of graphene is much lower. Thus, numerous electrical contacts formed among the stacked graphene sheets contribute to additional, considerable electrical resistance. Moreover, when graphene sheets are stacked in a planar manner, direct access to the active surfaces is severely restricted.

Control over the orientation or arrangement of a nanostructure can provide advantages and additional leverage for certain applications. For example, oriented 1D nanomaterials, such as carbon nanotubes (CNTs), can outperform non-oriented counterparts in specific applications. It has been shown that vertically-oriented

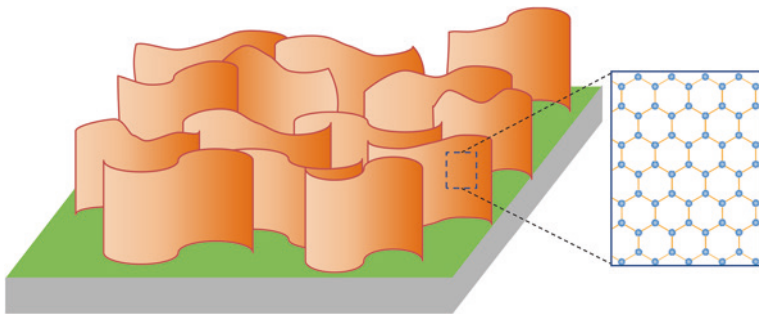


Fig. 2.2 Schematic of vertically-oriented graphene sheets

CNTs or CNT arrays have attractive characteristics as field emission electron sources for devices including flat panel displays, gas discharge tubes, and lamps [19]. When an electrical potential is applied between a CNT array and an anode, high local electric fields can be produced due to the very small radius of the CNT tip and the length of the CNT, which causes electrons to tunnel from the nanotube tip into the vacuum.

Similarly, when the orientation of graphene on a substrate is changed from being planar or horizontal (randomly oriented or parallel to the substrate surface) to being vertical (perpendicular to the substrate surface), i.e., to form VG (Fig. 2.2), it is promising to effectively harvest both intrinsic properties of graphene and additional characteristics due to the free standing arrangement.

2.3 Unique Properties of VG

In addition to general properties of graphene, VG sheets have some unique characteristics, making them significantly different in many aspects from the conventional horizontal, randomly oriented graphene sheets. And because of these unusual features, VG sheets possess a number of unique mechanical, chemical, electronic, electrochemical, and optoelectronic properties [20] that could benefit their potential use in a wide range of applications.

The first and probably most noticeable feature of VG sheets is the vertical orientation on the substrate, which improves the mechanical stability of graphene. While VG networks can have various morphologies, such as being petal-, turnstile-, maze-, and cauliflower-like [21–23], each VG nanosheet usually represents a free-standing, self-supported structure with rigid integrity by itself. This rigid structure preserves the mechanical stability of 2D graphene nanosheets, which would otherwise collapse and/or stack with each other in random directions, in part due to the strong van der Waals interactions. From the device perspective for electronic, optoelectronic, and electrochemical applications, the aligned structure of VG sheets can enable new designs and potentially improve the device

performance. For example, the alignment of highly conductive graphene planes in parallel with the direction of charge transport in devices can result in a higher device efficiency. The vertical arrangement of VG sheets also facilitates the characterization of VG by using a scanning electron microscope (SEM), since their lateral dimensions are much larger than their thicknesses.

The second feature of VG sheets is a non-agglomerated morphology with a high specific surface area (or surface-to-volume ratio) and abundant open channels between the sheets. This feature can be taken as a direct result of VG's vertically-oriented structure, but it has significant implications worth being elaborated upon. Because VG sheets are non-agglomerated or non-stacked, the entire VG surface area can be readily accessed by gas/liquid molecules or ions. This enhanced accessibility is very critical to the performance of sensing and electrochemical devices that require maximized accessible surface area. One of the main reasons that graphene has attracted strong interest is its extremely high specific surface area due to the atomic thickness. However, re-arrangement (e.g., stacking) of horizontal graphene nanosheets can easily lead to a significant decrease in graphene's available surface area. The difficulty and challenge to preserve graphene's accessible surface area can be minimized to a large extent by using VG as an alternative. By carefully choosing growth parameters (e.g., plasma source, pressure, etc.) in a PECVD process, it is possible to adjust the inter-sheet spacing between the neighboring VG nanosheets from a few tens to several hundred nm and even larger [24–26]. Taking the advantage of this non-agglomerated structure, the specific surface area of the VG networks could reach a high value of $\sim 1100 \text{ m}^2 \text{ g}^{-1}$ [27].

Third, VG sheets have long, exposed, ultra-thin, and reactive graphene edges, which are attractive for applications relying on the edge activity. An individual VG nanosheet typically has a tapered shape, i.e., its thickness reduces from a few-graphene layers at the base to being atomically thin at the top [28]. The thin graphene layers in VG usually have an interlayer (002) spacing between 0.34 and 0.39 nm [29] and can be stacked in the Bernal AB configuration. However, rotating and disordered stacking orders are more often found in few-layer graphene sheets [28]. Recently, it was revealed that most of the VG edges are made of folded seamless graphene sheets and that only a relatively small fraction of the edges remain open during the plasma-based growth [30]. These active edges can boost the chemical and electrochemical activity of VG for sensing and electrochemical applications.

Fourth, VG sheets grown on a conductive surface minimize electrical resistances of the entire graphene network, as the extremely high in-plane conductivity of graphene can be effectively used, avoiding sheet-to-sheet resistance, and the contact resistance between VG and the substrate can be significantly reduced. In fact, first-principles calculations revealed that VG could possess electronic properties very similar to those of suspended graphene and ensure high carrier mobility as most of the π electrons of graphene are free of disturbance [31].

These unique morphological and structural characteristics make VG very attractive for many emerging energy and environmental applications in addition

to the common field emission devices. For example, the large accessible surface area and high in-plane electrical conductivity can advance VG's use as a superior electrode material in various energy storage/conversion devices, such as supercapacitors, batteries, fuel cells, and dye-sensitized solar cells. The high density of open edges with controlled structural defects in VG can enhance the chemical and electrochemical activity and makes VG a promising sensing element for biosensors and gas sensors. The high aspect ratio and electrical conductivity of VG can facilitate the generation of atmospheric corona discharges with lower power consumption and reduced emission of hazardous ozone [32].

2.4 Summary

The properties of VG have been discussed in this chapter. Since VG is inherently graphene, general electronic and mechanical properties of graphene have been briefly introduced. On the other hand, being arranged perpendicularly to the surface of a substrate also induces a number of unique structural features for VG. These very unusual characteristics have been emphasized by comparing VG sheets with planar (or horizontal) graphene sheets. The unique properties of VG include: (i) improved mechanical stability owing to its vertical orientation; (ii) non-agglomerated morphology with a high specific surface area and abundant open channels; (iii) long, exposed, ultra-thin, and reactive graphene edges; and (iv) minimized contact resistance between VG and the substrate because of the direct growth of VG on a conductive surface. These features have made VG attractive for various applications.

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