

Chapter 1

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Introduction

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A new field of research in material science and condensed matter physics was formed after the synthesis of graphene in 2004 [1, 2]. This field is named Two-dimensional (2D) material due to the fact that graphene is a single atomic-layer crystal. The synthesis itself together with the phenomenal properties of graphene has led to a Nobel Prize in physics awarded to A. K. Geim and K. S. Novoselov [3]. Since then, the field is expanding with the involvement of researcher not only from young community, but also from experts who have been working on materials like graphite, fullerenes and carbon nanotubes which are strongly graphene related. In the last several years, researches focused on graphene and related topics increasing rapidly, see Fig. 1.1. While a part of these effects have been making to explore more on the graphene itself and its applications, some other parts were put on discovering new 2D materials. It has been evidenced from graphene, same material having different dimensionality can have different properties. Therefore, many materials with hidden properties which will only manifest itself at other dimensions yet to be discovered.

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On the other hand, with the advent of powerful supercomputer facilities, calculations that seems impossible to finish in a reasonable time now has been made accessible. At the same time, given the accuracy of the calculations is the most crucial aspect of computational physics, especially when the results are related to the prediction the real properties of materials, researchers and programmers have been making important progress to make sure theories and its implementation are correct and the results they yield are within acceptable precision. Equipped with these tools, theoretical predictions on the structure and the properties of material have served well on discovering unexplored features. Moreover, detailed characterizations at atomic

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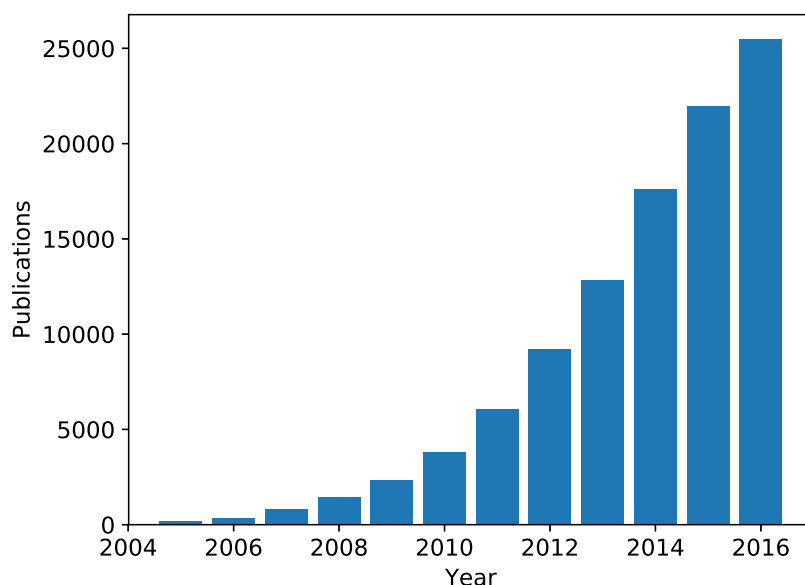


Fig. 1.1 Graphene related publications during the last decade. Data source: ISI Web of Science. ¹

scale benefits the experimental results to make it more convincing, or even sometimes to explain the unexpected results.

Considering all mentioned, it is a sound approach to apply the state-of-the-art computational methods that accompanied with high-performance supercomputer facilities to investigate the physical properties of novel 2D materials. This thesis is a summary of several works which has accomplished during my PhD study and were initiated to this end. The thesis is organized as followed: For the rest of this chapter, I will first introduce graphene and some post-graphene materials that discovered right after graphene and, briefly, methods used to synthesis 2D materials. The following [chapter 2](#) will present the computational methods, the theory behind and the implementations of them. In [chapter 3](#), I will discuss several general properties of 2D materials. The next two chapters will be the main results from my works. Starting from specific properties targeting at specific novel 2D materails in [chapter 4](#), and followed by modification of physical properties of 2D materials in [chapter 5](#). Conclusions for the thesis will be given in the last chapter.

¹This result is obtained by searching for "graphene" in the topic field of Web of Science.

1.1 Graphene

Graphene is composed of carbon (C) atoms arranged on a hexagonal lattice. Each C atoms bond to three neighbouring C atoms. Graphene is one single atomic layer of graphite, see Fig. 1.2. These layers in graphite are stacked on top of another through weak physical bonding, whereas within each layer C atoms are hold together by strong chemical bonding. As a result, it is possible to just isolate single layer from graphite without damaging the layer itself.

1.1.1 History

The story of graphene can be trace back to the discover of graphite around 1564 in England[5]. Ever since, people have been using the graphite, the tip of a pencil, for writing and drawing. The black trace left behind by pencil they are actually stacks of graphite and graphene, by chance even a single layer graphene can present. Apart from being a part of a pencil, graphite certainly has been holding a important position in technology and industry due to its rich chemistry, low friction, high electrical and thermal conductivity etc.. On the other hand, the synthesis of single layer graphene seems to be discouraged by both experimental and theoretical limitation. On the experiments, there are have been attempts[6, 7, 8, 9] to isolate graphene or ever grow it. However, they were mostly failed on control of the number of layers and identifying graphene itself. Addition to these experimental difficulties, on the theory, it was believed that strictly 2D material should not exist due to a divergence in the thermal fluctuation in 2D materials that will make them not stable [10, 11, 12]. Nevertheless, graphene was still considered as theoretical model. for example, Wallace [13] was the first one to study the band structure of graphene [14] and found some of the interesting properties like semimetallic band structure.

Although not in the form of graphene, the single atomic layer of graphite has been already seen and studied in other forms although includes certain type of characteristic defect that differ it from graphite, e.g. fullerene and nanotube, see Fig. 1.2. Flulerene is a C modelue has a quasispherical hollow ball shape. It is composed of both six- and five-folded C rings, where the latter give positive curvature and made closed surface possible which resemble a football[15, 16]. The Nobel prize in chemstry of year 1996 was award to Harold W. Kroto, Robert F. Curl and Richard E. Smalley for their discovery of fullerene. The method to produce a large quantity of fullerene, i.e. arc-discharge method[16], also results in another important carbon allotrope: carbon nanotubes[17].

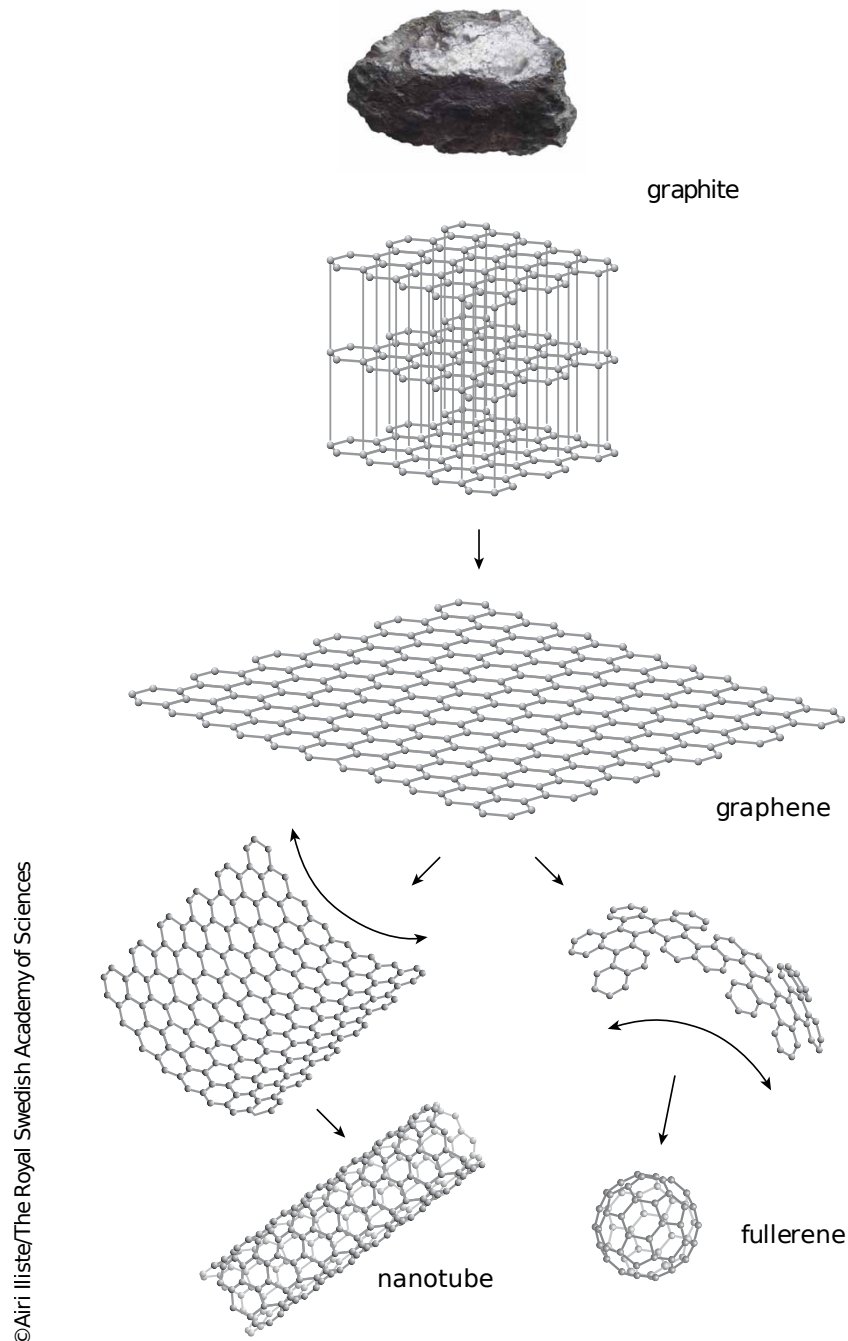


Fig. 1.2 Relation of graphite, graphene, fullerene and nanotube. Image source: the Nobel prize in physics 2010 [4].

Despite sharing similar production method with fullerene, carbon nanotubes are more close to graphene in a sense that it can be construct by rolling up finite graphene sheet into a hollow tube as its name suggested, and more importantly, these two both free of pentagonal C rings while fullerene must have a certain number. Carbon nanotubes are observed to have micrometer in lengths and nanometer in diameters and having either metallic or semiconducting nature depending on its edges. Individual nanotube has a Young's modulus of 0.64 TPa and it is 56 times stronger than steel wire[18].

In 2004, the situation has changed completely for graphene with the successfully isolated single layer graphene from graphite by A. K. Geim and K. S. Novoselov at Manchester University using a simple micromechanical cleavage method. The key ingredient, except for sophisticated experimental control, as compared to the previous failures[6, 7] in this case is that the Si wafer under the graphene made it easier to identify graphene[3]. The synthesis of graphene itself already is a ground-breaking achievement, however, what excited the researcher the most is the extraordinary properties of graphene. In the following section, I will summarized some of them to illustrate this point.

1.1.2 Physical properties

As mentioned previously, graphene is the single atomic layer of graphite. It posses an interesting structure with high symmetry which many of its properties are attributed to.

To understand this symmetry, we first need to discuss the hybridization of bonds. C atom has six electron, where two of them strongly localized near the nuclei core, they are called core electrons, such that their interaction with other electrons from other C atoms are suppressed. This only left us with four valence electrons to interact with others and then form bonds. As shown in Fig. 1.3, the s orbital will hybrid with p_x and p_y orbitals and form three equivalent sp^2 hybridized orbitals. They repel each other to have a maximum distance between one and the other. Therefore, an optimal angle between them is 120° , it will lead to the honeycomb structure of graphene. The p_z orbital left unchanged.

Now C atoms are ready for bonding. The results of bonding is shown in Fig. 1.4. One sp^2 hybridized orbital with another one from adjacent atom form strong σ bond, while p_z orbitals form π bonds. It may look like an alternative single and double bonds between atoms, actually the bond order in graphene is $4/3$ and it is uniform. We will talk about how a delocalized π bond is more stable than alternative single and double bonds in the later chapter where Clar's theory is discussed.

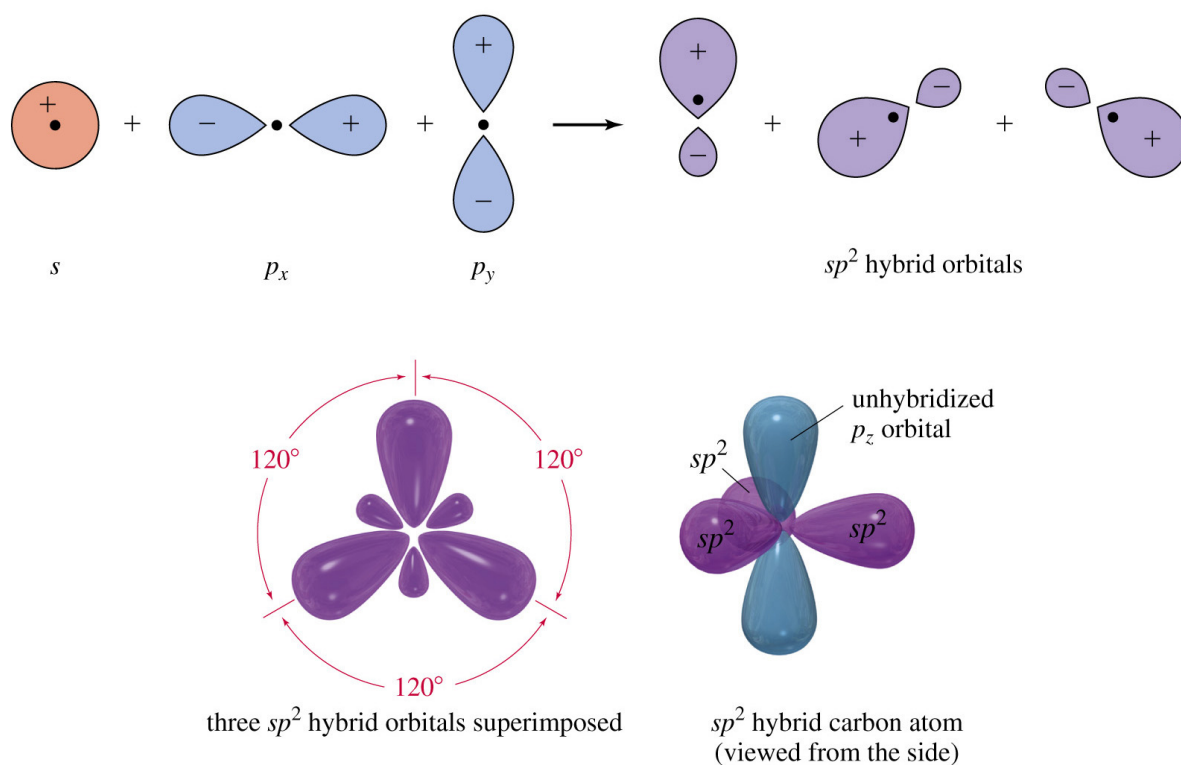


Fig. 1.3 The formation of sp^2 hybridized orbitals with unhybridized p_z orbital. Image source: [19].

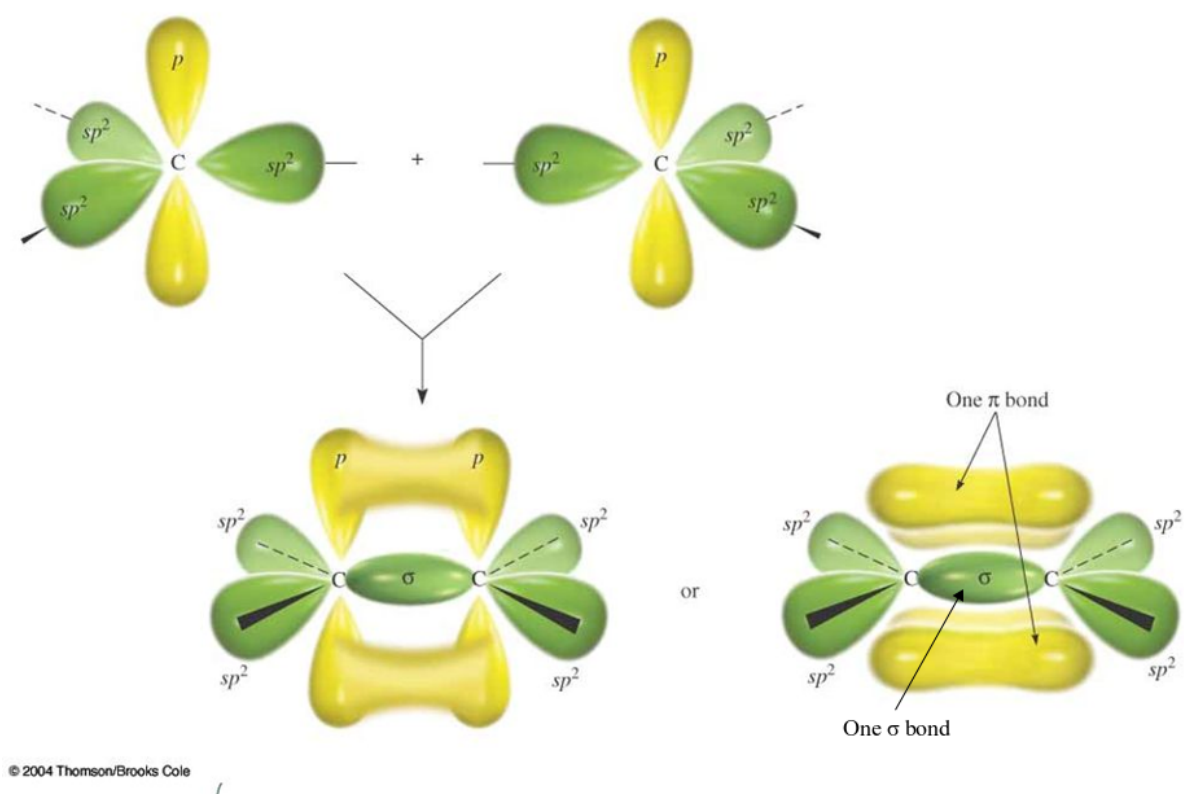


Fig. 1.4 The formation of sp^2 σ and p_z π double bond. Image source: [20].

Because of three-coordinated bonds, C atoms that are arranged in a honeycomb lattice², or a hexagonal bravais lattice with two atoms per site, see Fig. 1.5. Graphene has uniform bond lengths of 1.42\AA and uniform bond angles of 120° .

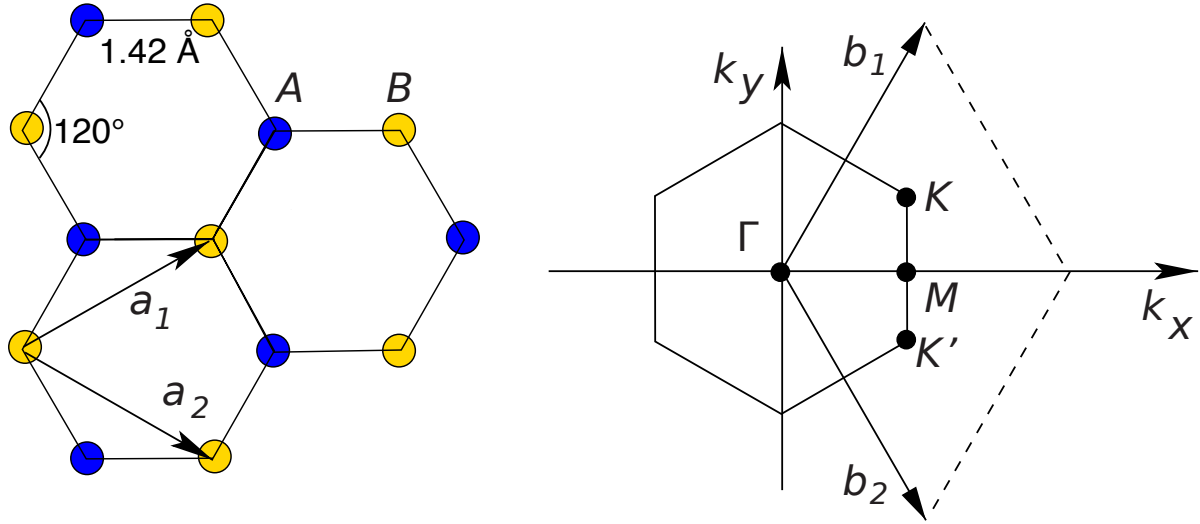


Fig. 1.5 Graphene lattice and its Brillouin zone. Image source: [14].

Every atom has same local environment, however, adjacent atoms are not equivalent. They belong to different hexagonal sublattices A and B as indicated with blue and yellow colors in Fig. 1.5. a_1 and a_2 are the basis vectors in real space connecting equivalent sites. b_1 and b_2 are the basis vectors in reciprocal space connecting equivalent k -points. The hexagon in the reciprocal space is the first Brillouin zone where all inequivalent k -points are contained. These k -points associate with different parallel lines of atoms and thus also indicate different directions in the real space. The k wave vectors near the Γ point have longer wave length, while those at the boundary of the first Brillouin zone have wave length that is two times the unitcell dimension on that direction. For example, the most interesting k -point for graphene is the K and K' points. These directions correspond to the a_1 and a_2 directions in real space. It is only at these k -points in the Brillouin zone, the antibinding and bonding π band touch each other. Further, the energy E dispersion with \mathbf{k} vector has a linear relation, $E = \hbar v_F |\vec{k}|$, around these points, where \hbar is reduced Planck constant and v_F is Fermi velocity (in graphene it is 10^6 m/s). Several consequences of this relationship can be summarized. First of all, electrons in graphene behave like photon, can be describe by Dirac equation for massless relativistic particles[21]. For this reason, the K and K' points are referred as Dirac points, its vicinities are called Dirac cone, and electrons

²honeycomb lattice is not a bravais lattice.

or holes can be described by relativistic. Secondly, the carrier concentration can be tuned continuously from electron to hole with a perpendicular electric field[3]. Thirdly, the carrier in graphene can tunnel through finite height potential it normally incident to without reflection—Klein tunneling[22]. Fourthly, under magnetic field, zero energy Landau level appears, and the large energy interval between zero to first level made it possible to observe quantum Hall effect at room temperature [23]. New phenomenon driven by the linear dispersion are not limited to these yet they are the most profound ones.

erpan: make the connection and finishing by listing other properties

As compared to π bond, σ bond originate from strong overlap of sp^2 orbitals. The interaction is strong and the splitting of bonding and antibonding orbitals are large. Which makes the σ bonding orbitals deep in energy, or in other word, makes it strong and difficult to break. This feature contribute the most to the mechanical strength of graphene which has a Young modulus $E = 1\text{Tpa}$ and intrinsic strength of 130 Gpa [24]. This marks the strongest material ever measured. More than 300 times stronger than steel and four times harder than diamond. On the other hand, p_z orbitals are less overlapped. This makes the π bond energy close to Fermi level, i.e. the highest occupied state. Therefore, they contribute the most to the electronic properties of graphene.

1.2 Post-graphene Materials

1.2.1 Functionized Graphene

Graphane

Fluorographene

1.2.2 Boron Nitride

1.2.3 Silicene and Germanene

1.2.4 Transition Metal Dichalcogenides

1.3 0D and 1D from 2D: buckyballs, nanotubes and nanoribbons

1.4 Synthesis methods

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