Physical Properties of Novel Two-dimensional Materials and Their Modifications

From first-principles studies

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I would like to dedicate this thesis

to my loving parents Arkin and Perwin,

to my beloved wife Adila Dilshat,
to my cherished sons Efran and Wildan.

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 65,000 words including appendices, bibliography, footnotes, tables and equations and has fewer than 150 figures.

Yierpan Aierken
April 2017

Acknowledgements

And I would like to acknowledge ...

Abstract

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Chapter 1

Introduction

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 leaded to a Nobel Price in physics rewarded 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 five years 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

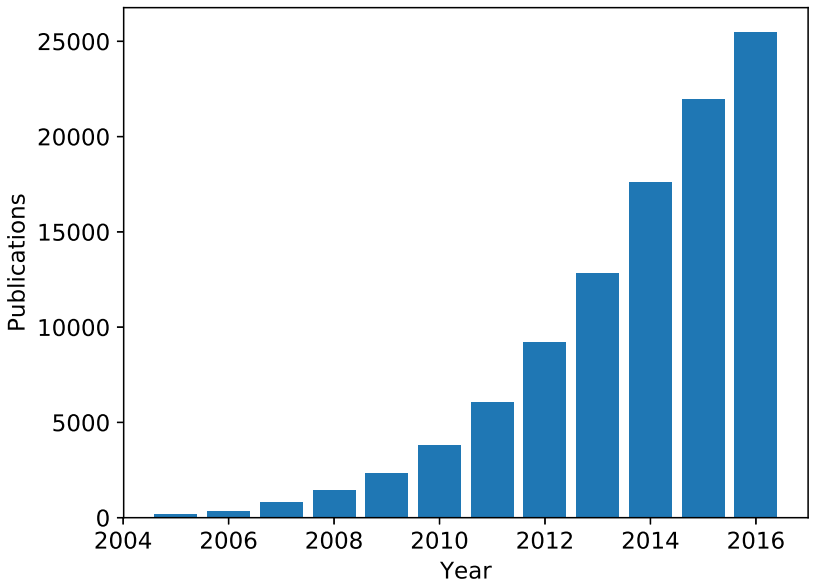

Fig. 1.1 Graphene related publications during the last decade. Source ISI Web of Science. [1]

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.

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

1.1 Graphene

Graphene is composed by 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. 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.

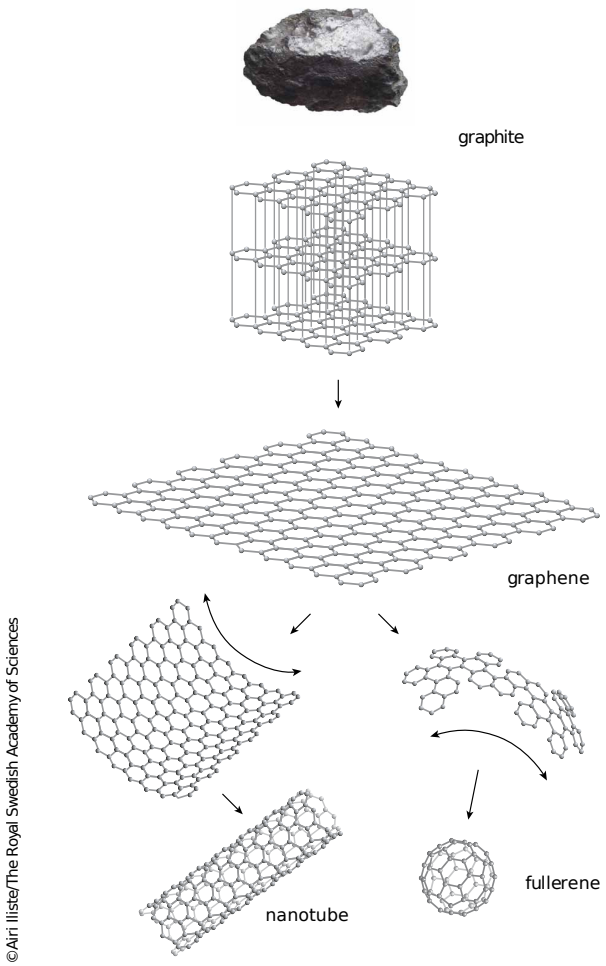

Fig. 1.2 Graphene related publications during the last decade. Source the Nobel prize in physics 2010 [4].

1.1.1 History and prediction

The story of graphene can be trace back to the invention of pencil in 1564, England[5]. Ever since people found that the graphite, the tip of a pencil, can leave a black trace when drawing on hard surface, they are making stacks of graphene, by chance even a single layer graphene.

1.1.2 Physical properties

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

Chapter 2

Computational methods

2.1 Theory

2.1.1 Density Functional Theory

2.1.2 Exchange-correlation functional

2.1.3 Jocob's ladder

2.2 Implementation

2.2.1 Basis set, Plane wave energy cut-off, K-points

2.2.2 Software Packages

Chapter 3

General physical properties 2D materials

3.1 Structural properties

3.1.1 Layer structure

3.1.2 sp hybirdization

Coulson's theorem

3.1.3 Isotropic v.s. Anisotropic monolayer

3.1.4 Multiphase allotropes

3.2 Electronic properties

3.2.1 Polar bond

3.2.2 Importance of crystal symmetry

Clar's theory

3.2.3 Importance of interlayer interaction

3.2.4 Accurate description from DFT

3.3 Vibrational properties

3.3.1 Phonon dispersion of 2D materials

3.3.2 Dynamic stability from phonon dispersion

3.4 Mechanical properties

Chapter 4

Results of Physical Properties Calculations in Novel 2D materials

4.1 Thermal properties

4.1.1 Thermal expansion and anharmonic oscillations

4.1.2 Quasi-harmonic approximation

4.1.3 Helmholtz free energy and specific heat

4.2 Piezoelectric properties

4.2.1 Piezoelectric constants

4.2.2 Importance of internal relaxation

4.3 Carrier transport properties

4.3.1 Carrier mobility

4.3.2 Deformation potential theory: non-polar materials

4.3.3 Deformation potential theory: polar materials

4.4 Magnetic properties

4.4.1 Magnetic ordering

Stoner criterion of ferromagnetism

4.5 Battery related properties

Chapter 5

Results of Physical Properties Modification in Novel 2D materials

5.1 Number of layers and types of stackings

5.1.1 Electronic properties

5.1.2 Vibrational properties

5.2 Mechanical strain

5.2.1 Carrier mobility

5.2.2 Magnetic properties

5.3 Adatom adsorption

5.3.1 Electronic properties

5.4 Heterostructures

5.4.1 Electronic properties

5.4.2 Li difusion

5.5 Defect induction

5.5.1 Structural properties

5.5.2 Electronic properties

5.5.3 Magnetic properties

Chapter 6

Conclusions

References

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[4] The Royal Swedish Academy of Sciences. *The Nobel Prize in Physics 2010 - Information for the public*. 2010. URL: https://www.nobelprize.org/nobel_prizes/physics/laureates/2010/popular-physicsprize2010.pdf (visited on 04/14/2017) (cit. on p. 3).

[5] H. Petroski. *The Pencil: A History of Design and Circumstance*. Knopf, 1990 (cit. on p. 4).

Appendix A

1

Appendix

2