

Molecular Morphological Influence of Graphene Related Carbon Materials on Their Electronic and Electrical Properties:A Theoretical Study
(**グラフェン関連カーボン材料の分子構造および電子・電気特性に関する理論研究**)

著者	Chutia Arunabhiram
号	53
学位授与番号	4033
URL	http://hdl.handle.net/10097/42447

ちゅていあ あるなびらん
 氏 名 Chutia Arunabhiram
 授 与 学 位 博士 (工学)
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 指 導 教 員 東北大学教授 宮本 明
 論文審査委員 主査 東北大学教授 京谷 隆 東北大学教授 浅井 圭介
 東北大学教授 久保 百司

論文内容要旨

Chapter 1 Introduction

Experimental and theoretical studies in the past have provided a treasure of information about the electronic and electrical properties of well structured graphene related carbon materials (GRCMs) such as graphite, fullerenes and carbon nanotubes. However more detailed studies are required for GRCMs with poor crystallinity such as carbon blacks, activated carbon, graphite oxide, soot, carbon fibers etc. This is because they have high values of industrial application such as in electronic components, cables, electrodes, electrode additives, tires etc. but, their structure and the basic understanding of the functionality of these materials have not been achieved fully [1]. In the present investigation a theoretical study is presented with the motivation to comprehend the influence of chemical morphology on the electronic and electrical properties of GRCMs.

Chapter 2 Computational Methods

A new method was developed by combining tight-binding (TB) method with molecular dynamics method to investigate the electronic and electrical properties of GRCMs. This method is ten million times faster than the conventional first-principles methods. In this new methodology combined tight-binding quantum chemical calculations and molecular dynamics (MD) simulations

were carried out, in this methodology first tight-binding method is employed to derive potential parameters to be used for MD simulations. Other theoretical methods used for this study are density functional theory (DFT) and time-dependent DFT.

Table 1. Binding energy and bond population of bonding and non-bonding atoms obtained from UA-QCMD and DFT

Properties	UA-QCMD	DFT
Binding Energy (eV)	-8.82	-8.12
Bond population		
Bonding atoms	1.06	1.09
Non-bonding atoms	-0.09	-0.17

Chapter 3 Validation of Methodology and Molecular Modeling

Prior to the investigation on the electronic and electrical properties of GRMCs the validity of the newly developed Ultra Accelerated Quantum Chemical Molecular Dynamics (UA-QCMD) method was checked. For validating this methodology a graphite structure with 64 atoms was considered and after the UA-QCMD calculations various parameters such as contribution of electrons in *s* and *p* orbitals, bond populations and binding energy was compared with DFT results (see Table 1). This

validated the newly derived potentials for the MD simulations.

Chapter 4 Influence of Cluster Size of Graphene Sheets on Electronic and Electrical Properties of Graphene Related Carbon Materials

Electrical conductivity of GRCMs is dependent on several factors such as conductivity of individual particles, degree of contact among the particles etc [2]. In this study first the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, HOMO-LUMO energy gap, chemical hardness and chemical softness of GRCM models were investigated, which provided an insight into their electronic and electrical properties. On estimation of electrical conductivity of these models, as shown in Figure 1, it was found that with the

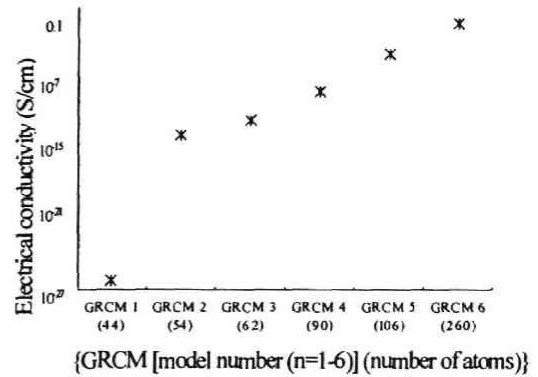


Figure 1 Electrical conductivity of versus systems

increase in cluster size the electrical conductivity significantly increased. Further, it was seen that on stacking the basic structural units the electrical conductivity was further increased. The basic reason for the enhanced electrical conductivity can be attributed to the increased number of π conjugations with cluster size or π -stackings of the BSUs. This work provided some of the fundamental explanations governing the electronic and electrical properties of GRCMs at atomistic level.

Chapter 5 Influence of Chemical Morphology of Graphene Sheets on the Electrical Properties of Graphene Related Carbon Materials

In chapter 5 for the first time a theoretical study on the influence of chemical morphology on the electrical properties of -OH and -SH modified graphene related carbon materials was carried out. It was seen that in the layered graphene models generated by stacking BSUs (see Figure 2) the energy gap shows a decreasing trend with increasing number of stacked layers. However, it is dependent on AAA stacking (where all atoms in the consecutive layers are above one another) or ABA stacking (where half of the atoms in the consecutive layers are directly above the center of the hexagonal ring and half directly over each other), patterns and on

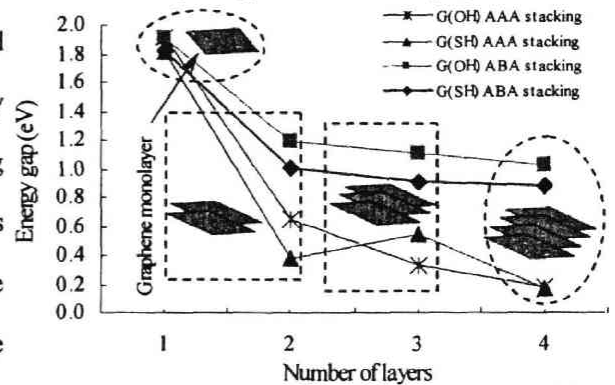


Figure 2 Energy gap versus number of -OH and -SH modified graphene (G) layers in AAA or ABA stacking patterns

the interactions between the stacked layers. For the oxygen modified graphenes the electronic properties were seen to be independent of the stacking patterns of the graphenes due to the higher electronegative nature of the oxygen atoms. In the sulfur modified graphenes the electronic and electrical properties are dependent on the stacking patterns. The reason for the anomalous behavior of sulfur modified graphenes is understood in terms of the interaction between the π -electron rich beds. It was seen that by engineering the interlayer distances between the graphene layers the electronic and henceforth the electrical properties of graphene related carbon materials can be altered. Estimation of electrical conductivity for larger models at different densities also revealed that electrical conductivity of the functionalized graphenes is dependent on the interlayer distances.

Chapter 6 Influence of Chemical Morphology of Graphene Sheets of Graphene Related Carbon Materials as Catalysts

Support for Pt Catalysts

To prepare and use heterogeneous catalysts deeper understanding of the nature of support and metal loading is required. In chapter 6, the adsorption of Pt₄ catalysts on functionalized graphenes was first investigated. It was theoretically shown that the adsorption of Pt on the graphene related carbon materials with oxygen containing groups are dependent on the concentration of these groups (Figure 3). This agrees with the experimental findings [2]. The fundamental reason governing the dependence of the favorable Pt adsorption on the concentration of oxygen containing group is due the electron density in the pristine graphene sheet. Higher concentration of oxygen containing groups results in the depletion of electron density which causes weakening of the anchoring capability of the π -sites towards Pt catalysts and results in the increase of adsorption energy. Since small or no HOMO-LUMO gap represents higher reactivity an analysis on HOMO-LUMO gap and chemical softness of all these systems was also carried out. It was clearly seen that adsorption of Pt₄ cluster on pristine graphene with an optimum number of -OH groups had the least energy gap and highest chemical softness among all the systems implying a high reactivity. This study provided the first theoretical evidence of the influence of chemical morphology on the adsorption Pt catalyst on graphene related materials.

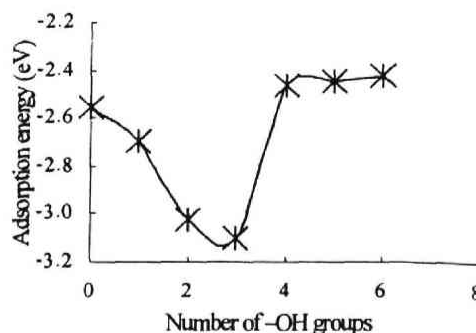


Figure 3 Adsorption energy of Pt on the ideal GRCM model

with the increase in the -OH groups

Chapter 7 Electronic and Electrical Properties of 1-D Organic Chains and their Composites of Rolled Graphene

Sheets

The first part of this investigation was focused on the study of the electronic and electrical properties of 1D linear organic chains namely alkenes with general formula C_nH_{n+2} with $n = 2, 4, 8, 10, 14$ and 16. It was seen that as the number of carbon atoms of these linear 1D organic chains increased they attained semi-conducting behavior. This was due to the increase in the number of π -electrons in the systems. This showed that sufficiently longer 1D organic C_nH_{n+2} systems would behave like semiconductors. A case study on the effect of doping on these systems was carried out with reference to C_8H_{10} system. It was seen that upon doping by bromine the conductivity of C_8H_{10} system was $\sim 10^9$ times higher than the undoped C_8H_{10} system (see Table 2). In this study for the first time quantitative estimation of

Table 2. Energy gap and electrical conductivity of C_8H_{10} , C_8H_9Br and $C_8H_{10}Br_2$

System	Energy gap (eV)		σ (S/cm)
	Calc.	Exp. ³	
C_8H_{10}	4.47	4.4	8.7×10^{-22}
C_8H_9Br	3.39	-	7.6×10^{-13}
$C_8H_{10}Br_2$	3.48	-	2.7×10^{-13}

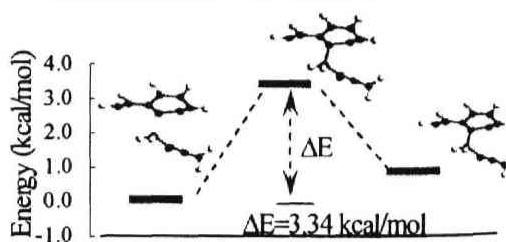


Figure 4 Energy level diagram showing energy barrier for the formation of (7, 0) CNT-C₄H₈ composites

electrical conductivity of all the C_nH_{2n+2} systems were reported theoretically. This work was further extended to the investigation of composite materials of C_nH_{n+2} ($n=4$) and (7,0) CNT. First the reaction mechanism for the formation of (7,0) CNT- C_4H_5 composite was carried out and a free radical reaction mechanism was proposed. TS calculation showed that energy barrier for the reaction is ~ 3.34 kcal/mol (Figure 4). Finally, a comparative study on the electronic and electrical properties of C_4H_6 , (7, 0) CNT and (7, 0) CNT- C_4H_5 was carried out. It was shown that the electrical conductivity of the (7, 0) CNT- C_4H_5 has an improved conductivity over both C_4H_6 and (7, 0) CNT systems. This study provided theoretical evidences that the electrical conductivity of CNTs can be tailored by grafting 1D organic chains to it.

Chapter 8 Summary and Conclusions

The present investigation has contributed to the science of GRCMs which reveals the fundamental aspects determining their electronic and electrical properties. This study also contributes to the chemistry of Pt adsorption on GRCMs providing theoretical evidence for the first time about the importance of oxygen containing groups in carbon materials as catalysts support. Furthermore, new composites materials of CNT-alkene systems were also proposed as a candidate for modifying electrical properties of CNT. This study has paved the way for a new field of computational chemistry concerning the study of GRCMs.

References: [1] Nakada et al. *Phys. Rev. B* **1996**, 54, 17954, [2] Coloma et al. *Langmuir* **1994**, 10, 750, [3] Gavin et al. *J. Chem. Phys.* **1978**, 68, 522.

論文審査結果の要旨

本論文は、グラフェン関連カーボン材料の分子構造および電子・電気特性を理論的に明らかにすることを目的として行われた。本論文は「Molecular Morphological Influence of Graphene Related Carbon Materials on their Electronic and Electrical Properties: A Theoretical Study (グラフェン関連カーボン材料の分子構造および電子・電気特性に関する理論研究)」と題し、以下の8章からなる。

第1章では、グラフェン関連カーボン材料の産業上における重要性について概説した後に、本論文で対象としたグラフェン関連カーボン材料の応用例と求められる機能に関する理解の現状について述べ、本論文の目的を明確にしている。

第2章では、本論文で用いた手法について説明している。具体的には、独自の Tight-Binding 理論に基づく量子分子動力学法と古典分子動力学法を組み合わせた量子論に基づく分子動力学法について述べている。また、妥当性の検証などに用いた密度汎関数法および時間依存密度汎関数法についてその理論を詳述している。

第3章では、Tight-Binding 量子分子動力学法に用いられるパラメータの妥当性の検証および分子モデリングについて述べている。Tight-Binding 量子分子動力学法のパラメータは、Tight-Binding 量子分子動力学法により計算された原子の電荷や結合エネルギーを密度汎関数法によるそれらの値と比較することで検証した。

第4章では、グラフェンシートのクラスターサイズが電子状態や電気特性に与える影響を Tight-Binding 量子分子動力学法に基づき調べている。グラフェンシート中のベンゼン環の数の増加とともに電気伝導特性が対数的に増加することが理論的に示された。さらに、グラフェンシートを積層することで電気伝導性が向上することも理論的に明らかにされた。

第5章では、グラフェン関連化合物の電気特性に与える化学組成の影響を調べる目的で、グラフェンシート末端をヒドロキシル基およびチオール基で修飾した積層カーボン材料の電気特性を調べている。具体的には、それぞれの修飾グラフェンシートの異なる積層構造における電気特性を調べ、積層構造・化学修飾と電気特性の関係を明らかにすることに成功している。

第6章では、グラフェン関連カーボン材料の固体高分子形燃料電池の電極触媒担体としての応用に焦点を絞り、白金触媒とグラフェンシートとの相互作用を電子レベルで調べている。さらに、エタノールを燃料とした際の白金上での酸化反応について量子論に基づく解析を行っている。

第7章では、アルキル鎖の電気特性に与える臭素ドーピングの影響を理論的に明らかにすることに成功している。さらに、アルキル鎖とカーボンナノチューブとの複合材料系の電気特性についても調べており、カーボンナノチューブの電気特性がアルキル鎖の修飾により制御可能であることを示すことに成功している。

第8章は、本論文の総括である。

以上、本論文は、量子論に基づく新規手法を活用することで、従来定量的理解が困難であったグラフェン関連化合物の電気特性に関して電子レベルでの新規知見を得ることに成功している。

よって、本論文は博士(工学)の学位論文として合格と認める。