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Theoretical Studies on Formation, Property Tuning and Adsorption of Graphene Segments

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1. Introduction

A single graphene sheet is a planar monolayer of $sp^2$-bonded carbon atoms arranged on a two-dimensional honeycomb lattice made of hexagonal rings. Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes and fullerenes. Planar polycyclic aromatic hydrocarbons (PAHs) with only benzenoid hexagonal rings can be viewed as fragments of a graphene sheet with the peripheral atoms saturated with hydrogen, and thus provide molecular models of graphene segments. Graphene segments are of paramount importance both from scientific and technological perspectives. Moreover, the PAHs or graphene segments themselves are of great research interest per se, since they are widely found in the residues of domestic and natural combustion of coal, wood, and other organic materials, and their unique electronic properties provide opportunities for novel functionalized nanomaterials and nanodevices (Wu, Pisula et al. 2007). Understanding the mechanism of formation of graphene segments is necessary to control its formation and in turn, to meet its application requirements. In our work, we have elucidated the role played by H during CVD growth of carbon materials (Zhang, Chu et al. 2000) including graphene and diamond. Graphene materials are endowed with a wealth of properties, including luminescence; which has been frequently reported in various CVD Diamond or a-C:H films (Bergman, McClure et al. 1994; Kania and Oelhafen 1995; Rusli, Amaratunga et al. 1995; Bourée, Godet et al. 1996; Liu, Gangopadhyay et al. 1997). Visible photoluminescence (PL) has been observed in carbon nanoclusters embedded in SiO$_2$ matrix (Zhang, Bayliss et al. 1996) and from C$_{60}$ thin films (Gapozzi, Casamassima et al. 1996). Unlike a-Si:H, the PL efficiency of a-C:H film is high and it shows luminescence even at room temperatures (Wagner and Lautenschlager 1986; Fang 1991; Schütte, Will et al. 1993; Xu, Hundhausen et al. 1993; Nevin, Yamagishi et al. 1994). A clear understanding of the luminescence phenomenon would help to produce high-quality luminescent films by a proper control of the experimental conditions. Correspondingly, the structure property relationship responsible for broadband luminescence in a:C-H films and carbon nanostructures was clearly pinpointed in our work (Zhang, Bertran et al. 1998; Feng, Lin et al. 2009). To the best of our knowledge, size-dependent PL mechanism was first reported by us (Zhang, Bertran et al. 1998).

The intermolecular, weak $n$-$n$ interactions are of utmost importance for understanding the various properties of graphene sheets (Novoselov, Geim et al. 2004; Feng, Lin et al. 2010).
and other carbon-related nanostructures, including hydrogen-terminated graphene nanoribbons with a finite nanosize width (Barone, Hod et al. 2006). The role of n-n interactions in benzene dimers (Feng, Lin et al. 2010) and in the stacking of graphene sheets (or graphene multilayers) have been thoroughly addressed in our detailed theoretical studies (Feng, Lin et al. 2009). In our investigations (Lin, Zhang et al. 2007; Fan, Zeng et al. 2009), the weak van der Waal’s (vdW) interactions were also found to be of pivotal significance in binding bio-molecules to carbon nanotubes (CNTs) from the viewpoints of important biological applications and bio-compatibility. These non-covalent, weak interactions do not affect the chemical and conductive properties of carbon nanotubes unlike covalent bonds and thereby aid an efficient retention of its pristine properties during their actual practical applications.

Water is a universal solvent and plays a crucial role in the mechanism of a variety of chemical and biological processes. The properties of water molecules or clusters in different ambiances can be a lot different from that of its bulk phase. To shed light on that, we have probed theoretically into the interaction of water clusters with graphite (Lin, Zhang et al. 2005). Single-walled carbon nanotubes (SW-CNTs) have novel structural, mechanical, and electronic properties but are hydrophobic. Water encapsulated within hydrophobic SW-CNTs, commonly known as ice nanotubes (INT), provide important clues to the functionality of biological nanopores (Sansom and Biggin 2001). Moreover, INTs have been found to exhibit novel properties such as proton conduction, hydrogen-bond network, phase transitions, etc (Maniwa, Kumazawa et al. 1999; Hummer, Rasaiah et al. 2001; Koga, Gao et al. 2001; Marti and Gordillo 2001; Noon, Ausman et al. 2002; Mann and Halls 2003; Marti and Gordillo 2003; Mashl, Joseph et al. 2003; Wang, Zhu et al. 2004). Through a systematic investigation, we have revealed the geometrical structure adopted by INTs within SW-CNT and the signatures in its vibrational spectra (Feng, Zhang et al. 2007).

Hydrogen is one of the most promising energy fuels for automobiles and can be potentially exploited in smaller portable devices. Due to the large surface area, carbon-based nanostructures, such as CNTs, appear to be ideal storage materials for the hydrogen storage. There is an ongoing debate within the experimental community with regard to the viability of CNTs as hydrogen storage materials. Our effective predictive modelling (Fan, Zhang et al. 2009) provides important and useful pointers to experimentalists on this. The chapter systematically organizes our computational findings pertaining to graphene segments into different sections, which is intended to provide a deep insight into the properties of graphene segments and useful guidance to future research and applications.

2. Graphene synthesis

A scientifically clear understanding of the different methods for graphene synthesis is essential to realize the optimum potentiality of graphene in a large variety of its applications. The size and quality of the graphene produced depends on the techniques used and the next sub-sections are devoted to some of the commonly used methods, their merits and demerits.

2.1 Chemical Vapor Deposition (CVD) approach

Synthesis of graphene by CVD has been introduced recently (Sutter, Flege et al. 2008; Li, Cai et al. 2009; Li, Zhu et al. 2009; Reina, Jia et al. 2009; Reina, Thiele et al. 2009). Graphene acquired from the CVD process has demonstrated large area, high quality, controllable
number of layers and low defects. CVD approach has been found to be by far the most effective technique to produce high quality, large scale graphene that can be compatibly integrated into the Si device flows.

The CVD based graphene synthesis process typically involves a thin layer of a transition metal (usually a few hundred nanometers thick) deposited on a substrate e.g. SiO$_2$. The substrate is then put into a furnace to be heated up to about 1000º C in a hydrocarbon gas (e.g. methane and hydrogen) environment. The transition metallic layer catalyzes the decomposition of hydrocarbon gas and the dissociated carbon atoms gradually absorbs into the metal layer or diffuses/remains on the metal surface depending on the metal. Experimentally, many different transition metal catalysts, (e.g. Ru, Ir, Pd, Ni, Cu) have been used to synthesize graphene and two distinct growth mechanisms have been proposed (Li, Cai et al. 2009). (I) Precipitated growth, in which decomposed C atoms dissolve into the catalyst first and then precipitate to the metal surface to form graphene during the subsequent cooling. This is because the solubility of carbon in the metal decreases with temperature and the concentration of carbon decrease exponentially from the surface into the bulk. The follow-up cooling process helps the carbon atoms to segregate to the metal surface to form graphene. (II). Diffusive mechanism, in which the decomposed C atoms remain or diffuse on the metal surface and then incorporate into graphene directly. Mechanism I corresponds to those metals that interact strongly with C atoms and has the binary phase of metal carbide (e.g., Ni) and growth mechanism II corresponds to those which have no metal carbide phase (e.g., Cu). For mechanism I, continuous precipitation of C from the interior of catalysts normally leads to the non-uniform, multilayer formation of graphene layer as carbon prefers to segregate at the nickel grain boundaries (Yu, Lian et al. 2008). This problem is alleviated in mechanism II (Li, Cai et al. 2009) and it is known to be the best for the synthesis of monolayer graphene. Notably, inch-sized graphene has been demonstrated and synthesized on the Cu foil surface (Li, Cai et al. 2009; Li, Zhu et al. 2009). A rapid cooling rate in mechanism I can aid the suppression of preferential segregation of carbon at grain boundaries of the metal (e.g Ni) and thereby control the number of graphene layers (Kim, Zhao et al. 2009), as demonstrated by Kim et al. Graphene segregation during cooling is a non-equilibrium process (mechanism I). Non-equilibrium segregation in general involves the transport of vacancy-impurity (vacancy-carbon in this case) complexes to sinks, such as grain boundaries and surfaces during cooling, and strongly depends on the cooling rate (Thuvander and Andrén; Yu, Lian et al. 2008). Different cooling rates lead to different segregation behaviors. Extremely fast cooling rate results in a quench effect in which the solute atoms lose the mobility before they can diffuse. A finite amount of carbon is found to segregate at the surface at medium cooling rates, which is found to be optimal. The extremely slow cooling rate allows carbon with enough time to diffuse into the bulk, so there will not be enough carbon segregated at the surface. Roughness of the metal substrates affects the uniformity of graphene layers synthesized by CVD (Yu, Lian et al. 2008). Thinner and more uniform graphene can be synthesized on smoother Ni substrates. Metal-catalyzed graphene synthesis has been very well studied. Yet, the role of H$_2$ in the growth atmosphere, which is also very crucial for graphene growth, needs to be addressed duly.

2.1.1 Role of H$_2$ during CVD growth

It is well-known that hydrogen gas plays a key role for CVD diamond growth, while it acts as an etchant for amorphous carbon. A hydrogen molecule is very stable at temperatures up
to 1000 °C. However, in the presence of a metal catalyst, at about 450 °C, the molecule dissociates and becomes reactive. Dissociation of the H$_2$ molecules in the presence of Ni and other metals was clearly demonstrated in an experiment done by Haluška et al. (Haluska, Hirscher et al. 2004). Atomic hydrogen then acts as an etching agent reducing preferably amorphous carbon that contains unsaturated dangling bonds. The role of etching by hydrogen during CVD is discussed in the following sub-section.

2.1.1.1 Etching by hydrogen during CVD

Diamond deposition with CVD has been successfully demonstrated using hydrogen as an etchant to remove the non-diamond phase. The selectivity of hydrogen in etching the two carbon phases, graphite and diamond, is considered the key factor for success in the synthesis of high-quality diamond films. The preferential etching of the sp$^2$ phase over the sp$^3$ phase by atomic hydrogen has been extensively reported. The role of atomic hydrogen both as sp$^2$ etchant and sp$^3$ promoter during the diamond growth is therefore well recognized experimentally and theoretically (Loh, Foord et al. 1996; Mendes, Corat et al. 1997). In addition, the etching selectivity of hydrogen has also been used to control the preferential growth orientation for obtaining oriented diamond crystals (Zhang, Jiang et al. 1997). Our comprehensive theoretical study based on Hartree-Fock (HF) molecular orbital approaches (Zhang, Chu et al. 2000) revealed the role of hydrogen species during the CVD growth and clarified the etching effect of the hydrogen species on sp$^2$ phase of carbon. The overlap between the Highest Occupied Molecular Orbital (HOMO) of one molecule and the Lowest Unoccupied MO (LUMO) of another (also known as electron delocalization) determines the nature of chemical reaction between the two molecules (Hoffmann 1988; Fukui and Fujimoto 1997). Because the extent of electron delocalization is inversely proportional to the energy difference between these MOs, a small energy difference between the HOMO of one molecule (electron donor) and the LUMO of the other (electron acceptor) indicates a favorable reaction. This energy difference between HOMO of the electron donor and LUMO of the electron acceptor is hereafter referred to as the HOMO−LUMO difference of the reacting system. The frontier orbitals (HOMO and LUMO) were determined in this work using HF and configuration interaction (CI) instead of density functional theory (DFT) because the latter theory provides too close occupied and unoccupied states to analyze. Under typical CVD conditions of diamond growth, hydrogen exists as various species of neutrals and ions. The HOMO-LUMO difference (with hydrogen as electron donor) as a function of the cluster size of two types of clusters is shown in Fig. 1. Each curve displays an overall tendency to decrease as the cluster size increases. This result is consistent with our earlier report (Zhang, Bertran et al. 1998) that the HOMO-LUMO gap of the same silicon or carbon cluster decreases as the cluster size increases and levels off when the cluster size reaches about 30 atoms. Thus, the reactivity of hydrogen species is less sensitive to the cluster size for larger clusters. The HOMO-LUMO differences between neutral hydrogen and all the clusters are illustrated in Figure 1(a), in which molecular hydrogen shows larger HOMO-LUMO differences and thus exhibits a lower reactivity than the atomic hydrogen. This relatively low reactivity of molecular hydrogen gives rise to the well-known small etching effect of molecular hydrogen in CVD processes (Harris, Doll et al. 1995). Being an abundant species in some CVD processes, atomic hydrogen is considered to act as the phase etchant. As illustrated in Figure 1(a), the HOMO-LUMO difference of H/sp$^3$-carbon is significantly different from that of H/sp$^2$-carbon, indicating that the reactivity of atomic hydrogen with the two carbon phases should be considerably different. The smaller HOMO-
LUMO difference of H/sp\textsuperscript{2}-carbon implies the preferential etching selectivity for the sp\textsuperscript{2} phase, which is in good agreement with experiments (Donnelly, McCullough et al. 1997; Ishikawa, Yoshimi et al. 1997).

Fig. 1. HOMO-LUMO differences between (a) neutral hydrogen species and (b) negative hydrogen species; and BN, carbon clusters as functions of atomic number (Zhang, Chu et al. 2000).

Fig. 1(b) shows the HOMO-LUMO difference of the H\textsuperscript{-} ion and the clusters. The result shows that the reactivity of the H\textsuperscript{-} ion is considerably higher than that of the neutral hydrogen. Similar to the case of neutral hydrogen, the H\textsuperscript{-} ion shows preferential etching of the sp\textsuperscript{2}-carbon over the sp\textsuperscript{3}-carbon phase. In fact, when the charged hydrogen ion approaches the carbon clusters, charge transfer may take place. This may lead to neutralization of the H\textsuperscript{-} ion and charging of the carbon clusters. Finally, the chemical reaction occurs between the charged clusters and neutral hydrogen. Hence, the reactivity of the hydrogen ion can also be explored from the point of view of charge transfer. Although it is impossible to obtain the HOMO-LUMO data for H\textsuperscript{+}, using the concept of charge transfer, the information about H\textsuperscript{+} may be indirectly studied by considering the reactivity between positively charged clusters and the atomic hydrogen. Table 1 lists the results on small charged clusters. Comparing with the neutral, the negatively charged cluster has its HOMO
and LUMO moved up. The energy difference between the HOMO of the negatively charged cluster and the LUMO of hydrogen is relatively small, indicating that the reactivity between the charged cluster and hydrogen is still higher than that between neutrals. For the positively charged cluster, the calculated HOMOs and LUMOs move to lower energies. The reactivity of atomic hydrogen (electron donor now) with the positively charged cluster is still higher than that with neutral cluster. Hydrogen ions also found in experiments have a higher reactivity than their neutral one (Davis, Haasz et al. 1987), which is in good agreement with our results.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆⁺ (sp²)</td>
<td>-0.55619</td>
<td>-0.23272</td>
</tr>
<tr>
<td>C₆⁺ (sp³)</td>
<td>-0.59758</td>
<td>-0.36760</td>
</tr>
<tr>
<td>C₆ (sp²)</td>
<td>0.05325</td>
<td>0.36703</td>
</tr>
<tr>
<td>C₆ (sp³)</td>
<td>0.20480</td>
<td>0.37316</td>
</tr>
</tbody>
</table>

Table 1. HOMO and LUMO Values of Small Charged Clusters in Comparison with Those of Neutral Ones, Obtained Using HF Method with Basis Set 6-31G** (Unit: au) (Zhang, Chu et al. 2000).

As shown in Table 2, the influence of carried charge on the HOMO and LUMO energies decreases as the cluster size increases. This suggests that charge transfer has only a minor influence on the larger clusters. Accordingly, the charge-transfer effect should have little influence on the conclusions drawn from the calculations for neutral species. We note that while charging might influence the sticking probability of the species with the substrate, the bonding characteristics between the two parties would be mainly determined by the reactivity between their neutrals. The interaction between hydrogen species and the substrate has two meanings: their sticking to the substrate and their chemical reaction with the substrate. The higher reactivity of the hydrogen ion implies a higher sticking probability with the substrate than for atomic hydrogen. In summary, atomic hydrogen and hydrogen ions show a higher reactivity than the neutral.

2.1.1.2 Prevention or minimization of etching

The effects of hydrogen can be turned around to the aid of synthesis and growth of graphene during CVD by a careful control of the growth conditions. Despite the etching action of hydrogen on the sp² phase of carbon, it is found that a critical amount of hydrogen is necessary to synthesize a few layers of graphene. This is because hydrogen maintains a balance between the production of reactive hydrocarbonaceous radicals and the etching of...
both mono and multi layered, is solely attributed to visible and efficient luminescence at room temperature in our comprehensive findings. Weak, intermolecular, vdW interactions and its importance have been thoroughly explored in our work. We have found the n-π weak vdW interaction to bind together the planar graphene segments or PAHs in bilayers and multi-layers over a large size range. Besides, in our theoretical studies, the weak interactions of graphene with some important bio molecules provide crucial clues to its possible bio applications. For instance, the encapsulation of water molecules within hydrophobic CNTs provides pointers to the capillary functionality of biological nanopores. We have practically ruled out the role of chirality of CNTs in binding H₂ molecules, while we have pointed out the role of curvature of CNTs in the same. This has important implications for the hydrogen storage potential of CNTs. Furthermore, we have highlighted the importance of weak interaction of CNTs with a few important biomolecules in preserving the chemical, electrical and other properties of the former. The weak interaction was found to enhance the electron transfer capabilities of some bio molecules in our study. This signifies the bio-compatibility of CNTs and its viability in different bio and other practical applications. A good understanding of the binding or interaction between bio-molecules and CNTs obtained from our work provides useful indicators for designing biosensors and drug delivery devices with bio-functionalized CNTs.

6. References


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The Stone Age, the Bronze Age, the Iron Age... Every global epoch in the history of the mankind is characterized by materials used in it. In 2004 a new era in material science was opened: the era of graphene or, more generally, of two-dimensional materials. Graphene is the strongest and the most stretchable known material, it has the record thermal conductivity and the very high mobility of charge carriers. It demonstrates many interesting fundamental physical effects and promises a lot of applications, among which are conductive ink, terahertz transistors, ultrafast photodetectors and bendable touch screens. In 2010 Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene". The two volumes Physics and Applications of Graphene - Experiments and Physics and Applications of Graphene - Theory contain a collection of research articles reporting on different aspects of experimental and theoretical studies of this new material.

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