厦门大学

博 士 学 位 论 文

C20 团簇组装固体材料及 C20 团簇在二维材料上的吸附特性研究

C20 cluster-assembled solids and adsorption of C20 on 2D materials

Muhammad Babar Hussain

指导教师姓名：朱 梓 忠 教 授
专 业 名 称：凝 聚 态 物 理
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摘 要

C_{60}具有优异的性能，如高温超导电性，因此它的发现激发了对碳团簇广泛的理论和实验研究。C_{60}超导的特性来源于电子-声子耦合，而电声子耦合会随着团簇尺度的减小而增大，因此寻找最小的富勒烯引起了极大的关注。在众多碳团簇中，C_{20}是最小、最简单并且是曲率最大的富勒烯结构。由于C_{20}电声子耦合比C_{60}强，因此可以预测C_{20}是高温超导的更好的潜在材料。因此，本文研究了基于C_{20}的团簇组装结构。另外，自从石墨烯问世以来，相比于其体相对应物而言，二维蜂窝状晶体由于其独特的对称性引起了广泛的兴趣。除了对这些纯二维材料本征性质的研究之外，吸附原子或者分子对这些二维材料带来的效应也得到极大的关注。由石墨烯和其他二维材料构成的复合体系将给实现材料电子特性或者光学特性的设计带来更多的机会。此外，基于富勒烯的异质结$(C_{20}/2D)$要求我们理解C_{20}吸附于各种二维材料时的物理本质，因为它们之间的界面相互作用和成键特性在异质结纳米材料的分子功能中扮演者重要的角色。因此，我们利用基于密度泛函理论的第一性原理方法研究了C_{20}吸附于二维材料诸如石墨烯，硅烯，锗烯，氮化硼，和二硫化钼时的性质。

本论文的第一部分主要研究的是由C_{20}团簇构成的晶体材料。通过基于密度泛函理论的第一性原理的计算，我们研究了由C_{20}团簇构成的晶体材料的结构，结合能和电子特性。一维时，当团簇头碰头时就可以形成一维分子晶体，我们研究了由不同C_{20}取向构成的两种一维分子晶体。我们还研究了将C_{20}排列成石墨烯结构时的情况。结果表明，在这种二维体系中，C_{20}是扭曲的并且以共价键的方式键连，由计算所得的能带结构以及态密度中可以看出该体系体现出金属性。对于三维体系，我们计算了由C_{20}构成的面心立方结构以及金刚石结构的情况。将C_{20}排列成金刚石结构时会产生C_{20}的二聚物，$(C_{20})_2$，它们之间可以存在很弱的范德瓦尔斯作用；能带结构以及态密度计算表明该材料为半导体材料，说明可以构成分子具体。然而C_{20}排列成面心立方结构时，相邻C_{20}分子之间强的相互作用使得体系表现出金属性而不是半导体性质。

本论文的第二部分，我们研究了C_{20}与二维材料，如石墨烯，氮化硼，锗烯，硅烯，锡烯和二硫化钼的相互作用。利用基于带范德瓦尔斯修正的密度泛函理论

的第一性原理计算，我们研究了 C_{20} 分子吸附在一系列二维衬底表面（石墨烯，氮化硼，锗烯，硅烯，锡烯和二硫化钼）时的结构性质和电子特性。对于每种情况，我们均考虑了三种 C_{20} 分子可能的吸附位，即顶位(T)、空位（H）和桥位(B)。我们的研究结果表明，C_{20} 与硅烯，锗烯，锡烯之间具有很强的吸附作用，而 C_{20} 与石墨烯，氮化硼和二硫化钼衬底之间只有很微弱的相互作用。电荷密度分析的结果表明 C_{20} 和硅烯，锗烯，锡烯之间有大量的电荷转移。分析表明，二维材料的褶皱结构在决定二维衬底与 C_{20} 的反应程度中取着重要的作用。

关键词：第一性原理；C_{20}；团簇组装的晶体；二维材料；吸附；C_{20} 二维异质结

Abstract

The discovery of fullerene C_{60} stimulated extensive theoretical and experimental studies of carbon clusters, because of its excellent properties such as high temperature carbon superconductivity. The possibility of superconductivity arising from electron-phonon coupling, and vibronic coupling becomes large as the cluster size decreases. So, tremendous attention has been focused to explore the smallest fullerenes. Among a variety of carbon clusters, C_{20} is the smallest and the simplest fullerene structure with the largest curvature. As a result, it can be predicted that the condensed form of the smallest fullerene C_{20} is the best potential candidate for high temperature superconductors because of its stronger electron phonon coupling than that of C_{60} fullerene. Thus in this dissertation, we have investigated various prospects of C_{20} based clustered assembled solid. Moreover, after the rise of graphene, two dimensional honeycomb lattices are recently materials of interest due to their unique properties as compared to their bulk counterparts. In addition to the studies on the intrinsic properties of these pure 2D materials, a great attention has also been paid to the effect of adsorbed guest atoms or molecules on some of these 2D materials. And the hybrid systems consisting of graphene and various two-dimensional materials would provide more opportunities for achieving desired electronic and/or optoelectronic properties. Moreover, fullerene based hetero-structure (C_{20}/2D) requires understanding on the nature of the adsorption of C_{20} on various two-dimensional materials because their interface interaction and bonding properties play important roles in molecular functionality in hetero-structure nanomaterials. Thus we have studied adsorption of C_{20} cluster on 2D structures, such as graphene, silicene, germanene, stanene, BN and MoS_2, by using first principal calculations based on density functional theory (DFT).

In part 1, the studies are mainly focused on solid made out of C_{20} cluster. By performing first-principles calculations based on the density functional theory, we have investigated the optimized structures, cohesive energies and electronic properties of crystalline solids made of C_{20} clusters. Two cases in one-dimensional (1D) with different orientations of C_{20} are studied. We found that 1D molecular solid could be formed when clusters are head to head. C_{20} arranged in 2D graphene structure are also

investigated. Our results show that, in this 2D case, C_{20} units are distorted and interlinked by covalent bonds, exhibiting metallic character which are supported by the corresponding calculated band structures and DOS profiles. In the 3D case, C_{20} arrangement in the face-centered cubic (*fcc*) and diamond structure are calculated. The optimized diamond structure composed of C_{20} molecules yields dimered C_{20}'s, i.e., $(C_{20})_2$, which are condensed by weak van der Waals interaction between $(C_{20})_2$ dimers. The band structures along with DOS calculations also suggest that molecular solid is formed in this case which is a semiconductor. However, for C_{20} in the fcc structure, there is significant coalescence of neighboring C_{20} fullerenes that makes system metallic rather than insulating.

In part 2, we have studied the interaction of C_{20} with 2D materials, e.g, graphene, silicene, garmanene, stanene, BN and MoS_2. We considered the geometric and electronic properties of C_{20} molecule adsorbed on these two-dimensional (2D) substrates by using first-principles calculations based on the density functional theory (DFT) with van der Waals correction. For each case, we have considered three adsorption configurations of C_{20} molecule, i.e. top-site (T), hallow-site (H) and bridge site (B), respectively. Our results show that C_{20}'s are strongly bound to silicene, germanene and stanene, however the adsorbed C_{20} molecules have only weak interactions with graphene, BN and MoS_2 substrates. Moreover, charge density plot implies substantial charge transfer taking place between the constituents of C_{20} and the substrate of silicene, germanene and stanene. Results indicate that the buckling structure of the 2D material plays important role in determining the reactivity of a 2D substrate.

Keywords: first-principles method；C_{20}；cluster-assembled solid； 2D materials；adsorption；C_{20} 2D-heterostructures
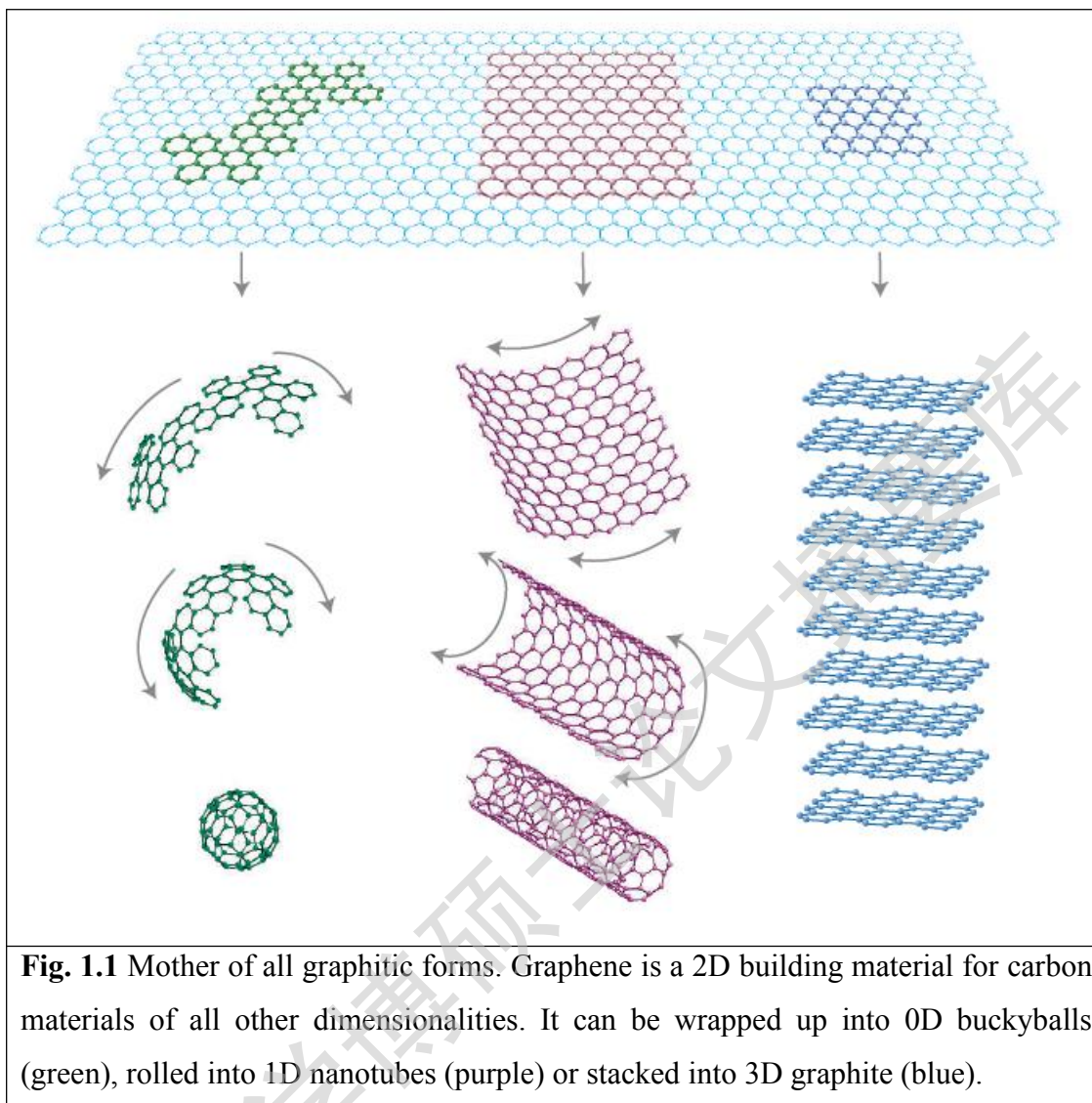
Contents

Chapter 1   Introduction

1.1 Development of fullerene structure

Carbon, the basis of life, is one of the most abundant elements found on earth and one of the frequently studied. It comprises the whole discipline of organic chemistry. A study of pure carbon would not seem all that exciting to most chemists. However, British chemist H. W. Kroto, and his colleagues, R. F. Curl, and R. E. Smalley, have made ground breaking history, and discovered a carbon molecule in 1985 which is know today as C_{60} Fullerene. They were awarded by the most prestigious award in the world, the Nobel Prize in chemistry in 1996[1].

It was third form of carbon after graphite and diamond which is the first known molecular form of carbon. Compared to diamond and graphite it is the molecular hallow alotrope of carbon. It is also called as Buckminsterfullerenes (buckyballs) that resembles the ball used in football (soccer). The structure of fullerene molecule C_{60} is a truncated icosahedron which has 32 faces, 20 hexagonal rings, 12 pentagons and 60 vertices. No pentagons share a vertex. It is shown in figure 1.1. The diameter (van der Waals) of a fullerene C_{60} cage is about 1.01 nm. The inter-nuclei diameter of a C_{60} fullerene molecule is about 0.71 nm. The hallow cage of C_{60} has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 0.14 nm. Each carbon atom in C_{60} molecule is covalently bonded with 3 neighboring C atoms [2].

The C_{60} molecule is extremely stable, withstanding high temperatures and high pressures. The exposed surface of the structure can selectively react with other species while maintaining the spherical geometry. Atoms and small molecules can be trapped within the molecule without reacting [3]. Because of the fascinating properties of fullerenes, they have broad range of applications such as in high-Tc superconductivity, modern microelectronics, bio-sensors, drug delivery, bio-film resistant surfaces, nano-bearings, mechanical reinforcement for membranes, artificial molecular motors, and polymer composites and consequently they have initiated new era of carbon nanotechnology [4-11].

Fig. 1.1 Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs (green), rolled into 1D nanotubes (purple) or stacked into 3D graphite (blue).

1.2 Brief introduction of C_{20}

Due to the interesting properties of fullerenes and their derivatives, search for new fullerenes sparked since the discovery of buckminister fullerene, C_{60}. Study of small carbon clusters is also important because the vibronic coupling becomes large as the cluster size decreases [12]. Among a variety of carbon clusters, C_{20} is the smallest one and has the simplest fullerene structure with 12 pentagons and no hexagon [13-15]. Tremendous attention has been focused on this the smallest fullerene, which has a closed shell carbon cage. C_{20} molecule is the smallest member of fullerenes family which has dodecahedral cage structure and obeys the Euler's theorem for fullerenes which is stated as fullerene molecules composed of twelve pentagons with varying number of hexagons.