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博士学位论文

基于单层二硫化钼的复合体系的
第一性原理研究

**First-principles studies of monolayer
MoS₂-based hybrid systems**

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摘 要

自从 2004 年石墨烯问世以来,它凭借其自身优异的物理化学性能已成为凝聚态物理, 半导体材料, 生物医学, 化学以及能源等领域的研究热点。近几年随着石墨烯材料在锂离子电池, 传感器, 半导体光电器件上的成功应用, 类石墨烯二维纳米材料的研究也逐渐受到了人们的广泛关注。其中二维层状过渡金属硫化物二硫化钼被认为是极具潜力的石墨烯替代物。单层二硫化钼除了与石墨烯一样具备极佳的导电性能和超强的硬度外, 该材料还具备发光性。此外, 单层二硫化钼本身具有直接带隙, 能够克服石墨烯, 硅烯, 锗烯等二维材料零带隙的缺陷。而且, 近期有研究显示, 由不同种类的二维材料结合在一起形成的复合体系, 其组分在性能上可以相互补充, 产生协同效应, 因而使复合材料具有更好的电子和光电特性。因此, 本文采用基于密度泛函理论的第一性原理方法对由单层二硫化钼以及其他类石墨烯材料组成的复合体系的结构稳定性和电子性质进行了系统的研究。

本论文的第一部分主要对单层二硫化钼的结构稳定性与基本电子性质进行了研究。首先, 我们对比分析了单层到多层二硫化钼的晶体结构, 原子间键长以及能带结构等。结果表明, 单层的二硫化钼是直接带隙半导体材料, 随着层数的增加, 直接带隙逐渐转变为间接带隙, 并且带隙逐渐变窄。当层数增加到五层时, 体系的能带结构已经与体相二硫化钼的能带结构基本一致。其次, 鉴于单层二硫化钼的直接带隙半导体特性, 我们又进一步研究了各类单原子在其面上的吸附。计算结果表明, 随着吸附原子的不同, 单层二硫化钼可以表现出金属性, 半金属性以及半导体性等不同性质。并且通过差分电荷密度图, 我们在某些原子吸附的单层二硫化钼上也观测到了局部或者长程的磁矩, 由此可见单层二硫化钼是一种比较易被修饰的二维材料。

在论文的第二部分, 我们研究了由单层二硫化钼和类石墨烯材料组成的超晶格体系的结构稳定性和电子性质。在这里, 我们选取石墨烯, 硅烯和锗烯这三种二维材料与单层二硫化钼进行交替堆叠。计算结果表明, 所有的超晶格均呈现出金属特性, 在费米能级附近原狄拉克点处的带隙被打开。通过分析超晶

格体系的差分电荷密度图，我们发现超晶格之所以显示出金属性，是因为在超晶格中原子层之间有少量的电荷转移。因此超晶格层与层间的相互作用，除了范德瓦尔斯相互作用之外，还有少量的离子性结合。

论文的第三部分中，利用带有范德瓦尔斯修正的密度泛函理论，我们对由单层二硫化钼和类石墨烯材料组成的异质双层结构进行了系统的研究。我们发现，由于石墨烯原子层和 MoS_2 中 S 原子层间的电荷转移，由单层二硫化钼和石墨烯组成的异质双层材料显示金属特性。而由硅烯或锗烯与单层二硫化钼组成的异质双层结构却是直接带隙半导体。而且，通过施加外应力或者改变原子层间距，我们可以调控异质双层结构的带隙类型及带隙大小。当我们对异质双层结构施加应力时，位于高对称 K 点处的带隙值会随着晶格常数的增大而减小。当应力由拉应力向压应力转换时，由硅烯和单层二硫化钼组成的异质双层结构可以维持其直接带隙，而由锗烯和单层二硫化钼组成的异质双层结构却会从直接带隙向间接带隙转变。当层间距小于平衡值时，带隙随着层间距的增大而增大；当层间距等于平衡值时带隙值达到最大值；而当层间距大于平衡值时，由于层间相互作用的减弱，带隙会随着层间距的逐渐增大而减小。我们的结果为基于单层二硫化钼纳米器件的设计提供了新的方法。

关键词： 第一性原理；单层二硫化钼；类石墨烯材料；复合体系；异质双层

Abstract

Since its discovery in 2004, graphene has become a hot research topic in condensed matter physics, semiconducting material, biomedicine, chemistry, energy and other fields, due to its excellent physical and chemical characteristics. In recent years, with the successful application of graphene in Li-ion batteries, temperature sensor and semiconductor optoelectronic devices, the graphene-like two dimensional nanomaterials have also continuously attracted a great deal of interests. Among them, the two-dimensional layered transition metal sulfides molybdenum disulfide (MoS_2) is regarded as a promising substitute of graphene. Apart from the properties that are distinct in graphene, such as marvelous electric conductivity and excellent hardness, the monolayer MoS_2 can also exhibit strong luminescence. In addition, the monolayer MoS_2 is a direct band gap intrinsic semiconductor, which could overcome the zero band gap limitation in graphene, silicene and germanene. Thus, in this dissertation, we systematically investigated the structural stabilities and electronic properties of hybrid systems composed of monolayer MoS_2 and graphene-like materials by using the first-principles calculations based on the density functional theory (DFT).

In part I, the studies are mainly focused on the electronic properties of monolayer MoS_2 . Firstly, we compare the structural parameters and band structures of systems with different number of layers of MoS_2 . Differing from its bulk form, the MoS_2 monolayer is a semiconductor with a direct band gap of 1.8~1.9 eV at the K-point. As the number of MoS_2 layers increases, the system transforms gradually from direct to indirect band gap semiconductor, and the band gap decreases. Then, single atomic adsorption of different atoms on pristine two-dimensional monolayer MoS_2 are systematically investigated by using density functional calculations with van der Waals correction. It is found that, upon adsorption of different type of adatoms, metallic, semimetallic or semiconducting behavior can be found on the adsorbed monolayer MoS_2 . Additionally, local or long-range magnetic moments of

two-dimensional MoS₂ sheet can also be attained through the adsorption, showing that MoS₂ could be a material suitable for functionalization.

In part II, the geometric and electronic structures of the superlattice consisting of graphene, silicene or germanene and monolayer MoS₂ have been studied by using density functional theory. Our results revealed that all superlattices exhibit metallic electronic properties. Small band gaps are opened up at the K-point of the Brillouin zone for all the four structural models. Furthermore, a small amount of charge transfer between layers in superlattices is found. Results indicate that the interaction between the stacking sheets in the superlattice is more than just the van der Waals.

In part III, we investigate the electronic properties of the hetero-bilayers (basic unit of a superlattice) composed of monolayer MoS₂ and graphene, silicene or germanene. Our results show that graphene-MoS₂ bilayers exhibit metallic electronic properties. However, both the silicene-MoS₂ and germanene-MoS₂ hetero-bilayers are direct band gap semiconductors. Moreover, tunable band gaps in silicene- and germanene-MoS₂ can be realized by changing the interlayer distance or employing in-plane compressing/stretching. The value of band gaps at the K-point decreases monotonically with the increase in lattice parameters. Meanwhile, through compressing or stretching, germanene-MoS₂ bilayers realize a transformation from an indirect band gap semiconductor to a direct band gap semiconductor, while the Silicene-MoS₂ bilayers can retain the direct band gaps. When the interlayer distance is shorter than the equilibrium value, the band gap increases with the increasing interlayer distance. Then the gaps reached their maximum value at the equilibrium state. After that, the band gap decreases with the increasing interlayer spacing, due to an increased interaction between the adjacent layers. Our results in this work provide a new method for designing MoS₂-based nanodevices with controllable band gaps.

Keywords: First-principles method; Monolayer MoS₂; Graphene-like materials; Hybrid systems; Hetero-bilayer

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