A First-Principles Study on a Graphene-Silicon System

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Abstract. Graphene and Silicon both are promising anode material for lithium-ion batteries, which has attracted considerable attention. The structure of Graphene-Silicon (Gra/Si) system has been investigated using density functional theory (DFT). We calculated the band structure, density of states (DOS) and electron density of the Gra/Si hybrid system. Our results show that the carbon component in the Gra/Si composites can enhance the conductivity of the whole material, and this special structure is promising to be applied in Li-ion batteries and other fields, such as sensing, catalysis and supercapacitors. The fundamental findings from this computational work will contribute to a better understanding of the properties and performance of Gra/Si system as LIB anode materials.

1. Introduction

As a naturally abundant element, Silicon is a promising anode material for lithium-ion batteries (LIBs), due to the highest theoretical specific capacity among all exiting anodes, which can reach 4200mAhg^{-1} in the form of Li$_{4.4}$Si [1, 2].Unfortunately, major obstacle hindering practical application of silicon anode is associated with its large volume change during cycles of charging/discharging, resulting in quick capacity fading and short cycle life [3, 4]. Various approaches have been employed to overcome this obstacle and to improve the overall electrochemical performance of Si-based anodes in rechargeable LIBs [5].

Graphene has attracted enormous attention because of its two-dimensional (2D) crystal structure with atomic thickness, unique electronic structure, high intrinsic mechanical strength, high surface area, and superior electronic conductivity [6]. Several groups have reported silicon core-hollow carbon shell structure, called also yolk-shell structure, and demonstrated in various degree of performance improvement [7, 8]. Graphene could be superior to other carbon materials as a contact with Si active materials in rechargeable LIBs and to effectively prevent the volume expansion/shrinkage and aggregation of Si phase during the Li charge/discharge processes [9-14]. However, thus far, there has been no comprehensive study as to the electrochemical mechanism at atomistic-scale.

In this work, We calculated the band structure, density of states (DOS) and electron density of Gra/Si hybrid system and this special structure is promising to be applied in Li-ion batteries and other fields, such as sensing, catalysis and supercapacitors.

2. Computational Method

All calculations have been carried out with the CASTEP module[15] of the Materials Studio software. The generalized gradient approximation (GGA)[16] Perdew-Burke-Ernzerhof (PBE) [17]functional has been used to accurately describe the interactions between an adsorbate and various surface. An energy cut off 300 eV was applied for the plane wave expansion of the electronic. A vacuum of 15Å between

the layers was considered. G-point sampling was used and with 3×3×1 K point for the integration of Brillouin zone.

In order to minimize the lattice mismatch effects between Silicon and graphene, we have considered a surface (or interface) periodicity of 2×2 and 3×3 for the Silicon and graphene. The dimensions of the unit cell we used in this study were 7.53 Å × 7.53Å × 26.1 Å. A full geometry optimization is performed till the force on each atom is less than 10^{-2}eV/Å, and the energy convergence with the energy difference is below 10^{-5}eV between consecutive self-consistent steps.

3. Result and Discussion

Initially, the geometry of the Gra/Si hybrid system was fully optimized without any fixed atoms on graphene or Si. The structure of the Gra/Si system was shown in Figure 1.
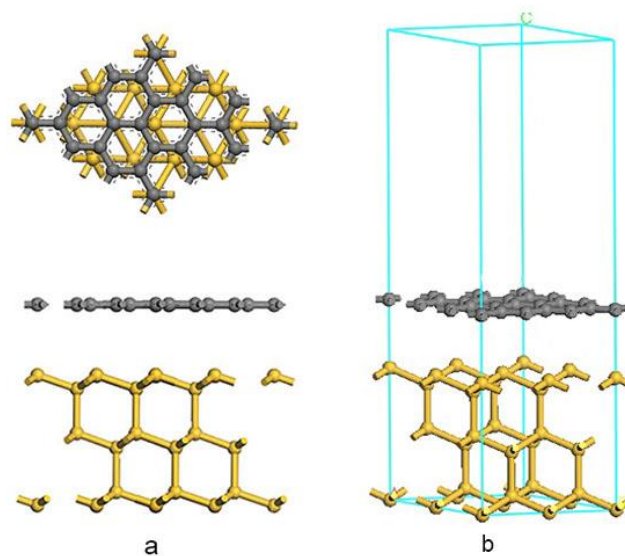

Figure 1 The structure of the Gra/Si system: (a) top and side view of Gra/Si; (b) Unit cell of the Gra/Si system

As shown in Figure 2a, the structure was stable after 16 iterations, and the energy of the equilibrium state is -5356.80 eV. The tolerances of total energy convergence, max ionic force and max ionic displacement we set are 0.1000E-04 eV/atom, 0.3000E-01 eV/Å, 0.1000E-02Å, and respectively, the calculated results are 1.597738E-006 eV/atom, 2.120132E-002 eV/Å, and 4.091334E-004 Å. It is obvious from the Figure 2b that all the values of the results are below our set value, which suggest that the results are meet the computational accuracy.
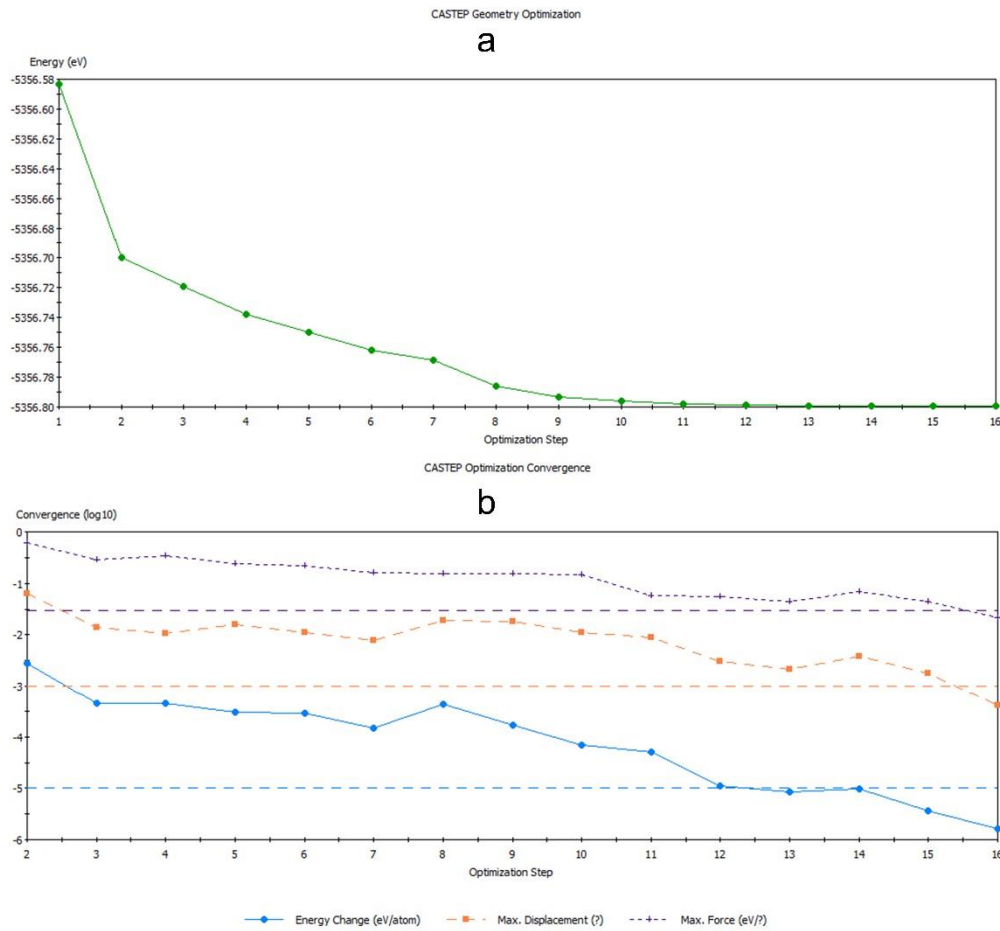
Figure 2 The step of optimization (a) geometry optimization, (b) optimization convergence
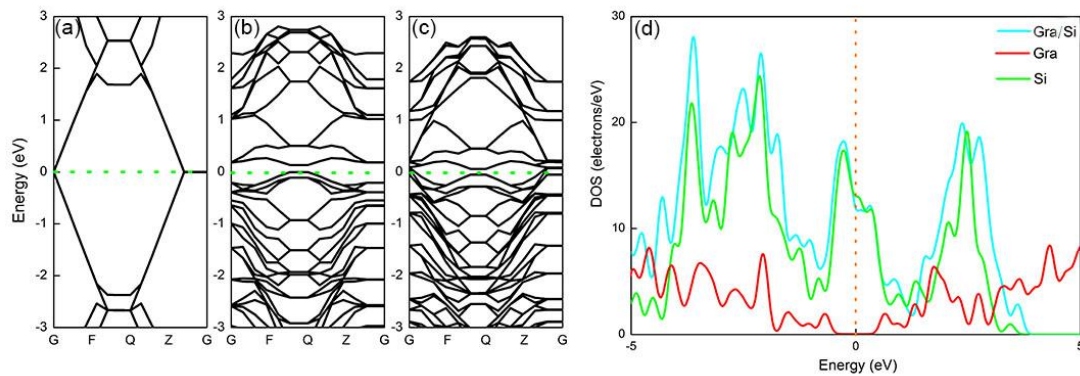

Figure 3 Band structures of (a) Graphene (b) Silicon (c) Gra/Si, and the DOS of Gra, Si, and Gra/Si.

The band structures of graphene and Gra/Si system are shown in Figure3. In these band structure representations, the Fermi levels are shifted to 0 eV. Since the Gra/Si system is maintained through dispersion interactions, the hybrid system retains the characteristics of its components.
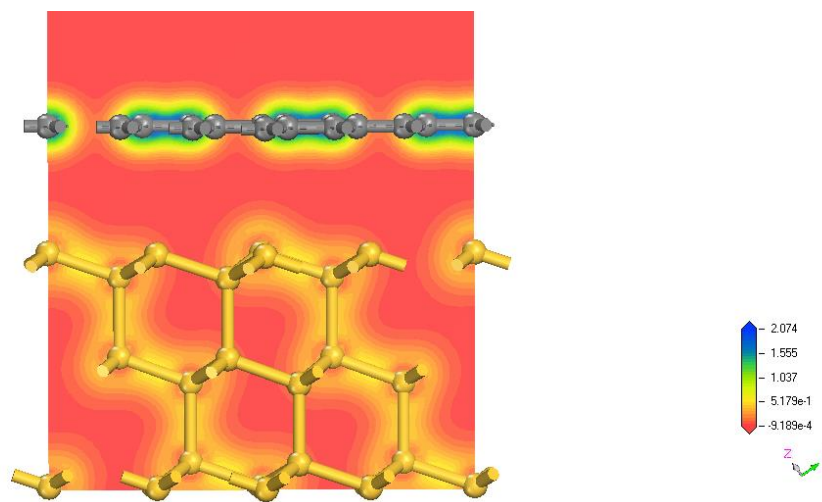
Figure 4 Electron density of the Gra/Si system

The calculated electron density on the best fit plane for Gra/Si system is presented in Figure 4. What we can know from the result is that the carbon atoms of graphene are surrounded by higher electrons, indicating that the carbon component in the Gra/Si composites can enhance the conductivity of the whole material. On this point, Gra/Si system is promising to be applied in Li-ion batteries and other fields, such as sensing, catalysis and supercapacitors.

4. Conclusions

The structure of Gra/Si system has been investigated using density functional theory (DFT). We calculated the band structure, density of states (DOS) and electron density of the Gra/Si hybrid system. Our results show that this special structure is promising to be applied in Li-ion batteries and other fields, such as sensing, catalysis and supercapacitors. The fundamental findings from this computational work will contribute to a better understanding of the properties and performance of Gra/Si system as LIB anode materials.

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