



Effects of interfacial structure and polarity on charge transfer between carbonaceous nanomaterials and rutile (110) surface



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ABSTRACT

The interfacial charge transfer properties of rutile (110) surface and two carbonaceous materials (graphene and C_{60}) are investigated by employing first principles calculations. Results show that electrons can be transferred from oxygen-deficient or negatively-charged rutile (110) surface to graphene whereas few electrons are transferred from neutral rutile (110) surface to graphene. For the interface between C_{60} and rutile (110), a significant charge transfer is also found from oxygen-deficient rutile (110) to C_{60} , while charge transfer levels from negatively-charged rutile (110) to C_{60} are analogous to that from neutral rutile (110) to C_{60} . The partial densities of states (PDOSs) show that such carbonaceous materials can induce negatively-shifted conduction bands of rutile (110).

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1. Introduction

The dye-sensitized solar cell (DSSC) has recently received considerable attention due to their ease of fabrication and cost-effectiveness compared with silicon-based photovoltaic devices [1–3]. Not only that, the nanostructured TiO_2 film is introduced into anode electrodes of solar cells for the first time, which achieves the separation of light harvesting and charge transport [4], whereas all other known photovoltaic devices perform both operations simultaneously. Therefore, a detailed investigation on charge transfer efficiency of semiconductor materials is quite valuable for improving conversion efficiency of dye-sensitized solar cell. Currently, survey of semiconductor materials focuses mainly on titanium dioxide (TiO_2), and the surface modification of TiO_2 is a popular research strategy [5–7]. A significant improvement in transport properties of TiO_2 surface has been achieved through doping with metal atoms or compositing with another semiconductor [8,9]. Especially, graphene film has been considered as the most promising nanomaterial for electrodes in dye-sensitive solar cells, due to its continuous, highly flexible, and transparent properties, etc. [10–12]. In 2010, it has been reported simultaneously by three groups that the graphene/ TiO_2 composite could greatly enhance the conversion efficiency of DSSC [13–15]. However, Zhang and co-workers claimed that graphene has the similar performance with other carbonaceous nanomaterials such as fullerene and nanotube, when these carbon materials combined with TiO_2 , respectively [16]. Imahori et al. has also found that the donor-ful-

lerenes deposited on the titanium dioxide surface exhibit efficient photocurrent generation [17]. However, the influence of the interfacial structure and polarity between carbonaceous nanomaterials and TiO_2 on conversion efficiency of DSSC is still not well understood. Hence, it is extremely necessary and meaningful to accurately construct these carbonaceous nanomaterial/ TiO_2 composite systems, and explore the nature of charge separation and transport at their interfaces.

In the present work, we systematically investigate geometrical and electronic properties of the graphene/rutile (110) and C_{60} /rutile (110) composite nanomaterials by employing first-principles theory. Several physical properties such as charge populations, binding energies, work functions, density of states, and electrostatic potential are calculated in order to obtain insight into their interfacial charge transfer. Finally, the intrinsic reason for enhancing the conversion efficiency of DSSC is revealed, and the details are as follows: (1) the weak interaction between TiO_2 and graphene hardly affects electrical conduction property of graphene, giving rise to the fact that graphene as charge carrier will promote charge transport; (2) the low conduction bands of composite systems increase the injection efficiency of the dye electrons; (3) the positive electrostatic potential of graphene tends to attract the additional electrons of TiO_2 surface, resulting in a quick charge separation and little charge recombination.

2. Calculation details

All of the DFT calculations were performed using plane-wave pseudopotential method, as implemented in CASTEP module in

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Materials Studio5.5 [18]. The general gradient approximation (GGA) with PBE functional [19] and the ultra soft pseudopotential [20] were used to describe the exchange correlation effects and electron–ion interactions, respectively. The wave functions were expanded into a basis set of plane waves with a kinetic energy cut-off of 500 eV. The Monkhorst–Pack grid [21] with $2 \times 2 \times 1$ k -point in the Brillouin zone was used for the geometrical optimizations and electronic properties calculations. The self-consistent convergence accuracy was set at 2.0×10^{-5} eV/atom, the convergence criterion for the force between atoms was 5×10^{-2} eV/Å, and the maximum displacement was 2×10^{-3} Å. Based on the optimized structure, the LDA+U approach [22] was utilized for electronic properties investigation of negatively-charged and oxygen-deficient composites systems. Hubbard values, U is critical, if $3.0 \leq U \leq 6.0$ eV, both electrons are localized on different Ti atoms [23]. Since Morgan et al. had used U value of 4.2 eV to reproduce the experimentally observed position of vacancy induced band gap [24], in this work we followed them and also used U value of 4.2 eV to oxygen-deficient system. Two negative charges were distributed in the model of negatively-charged system, and one oxygen vacancy was set in the oxygen-deficient system.

The optimized lattice parameters were found to be $a = 4.664$ Å and $c = 2.963$ Å for rutile bulk, in good agreement with experimental values ($a = 4.594$ Å, $c = 2.959$ Å) [25,26]. The rutile (110) surface was modelled using a slab model ($a = 14.795$ Å, $b = 12.993$ Å) with 5×2 surface unit cell periodicity, containing 155 atoms. Then the orthorhombic lattice with 6×3 graphene unit cell ($a = 14.760$ Å, $b = 12.783$ Å) was utilized to match with the rutile (110) model above. As a result, The graphene/rutile (110) composite nanomaterials were constructed according to an orthorhombic cell with periodic boundary conditions of dimensions 14.78/12.89/25.14 ($x/y/z$) Å, in which the interspaces of monolayer graphene or C_{60} and rutile (110) both were 2.0 Å along the z direction. The vacuum layer was located above graphene monolayer along c axis in the supercell for separating the adjacent unit, and the depth of the vacuum layer was 20 Å.

3. Results and discussion

3.1. Mode building of graphene/rutile (110) composites

Since an accurate composite model requires a choice of unit cell where the introduced strain is minimal, we chose an orthorhombic unit cell with lattice vectors of $a = n_r \cdot 2.96$ Å, $b = m_r \cdot 6.49$ Å, $c = 5.22$ Å for rutile (110) surface. Another orthorhombic cell with lattice vectors of $a = n_g \cdot 2.46$ Å, $b = m_g \cdot 4.26$ Å, $c = 5.22$ Å is also used for graphene monolayer, n_r , m_r , n_g , and m_g all are integers controlling the size of the unit cell. The graphene monolayer is next placed on the top of the (110) surface of rutile parallel to the [100] and [120] directions in graphite. When $n_r = 5$, $n_g = 6$, $m_r = 2$, and $m_g = 3$, two materials (graphene and rutile (110)) are the best lattice match. The average lattice type is still orthorhombic unit cell with lattice parameters of $a = 14.87$ Å, $b = 12.89$ Å, $c = 25.44$ Å. Along the [100] and [010] directions, the stretch strain of the graphene layer is 0.14% and 0.84%, respectively. Calculated band structures show that there is little difference between the strained cell and original cell (shown in Fig. 1), indicating that the strain produced by average cell slightly affects the electronic properties of graphene. Although the k -path of the orthorhombic lattice is different from that of traditional hexagonal lattice, the Dirac point of graphene still can be observed in orthorhombic unit cell. It should be stressed that the band structures of graphene in orthorhombic unit cell agree well with the previous report [27].

In order to investigate the influence of rutile (110) surface structure and polarity on charge transfer between graphene and

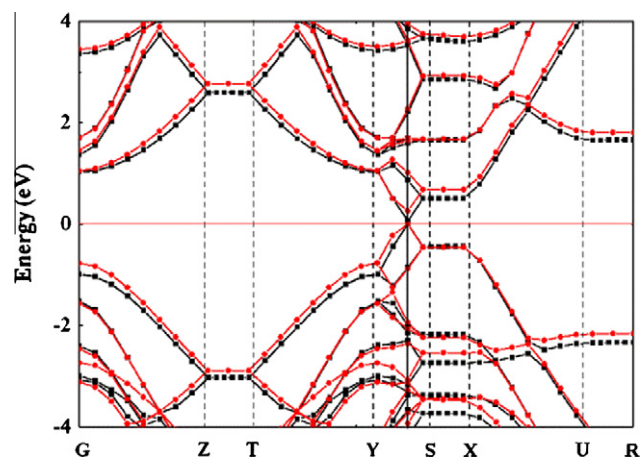


Fig. 1. Band structures of graphene in orthorhombic cell, n_g and m_g are equal to 6 and 3, respectively. The black curves show the case where there is no strain in the graphene layer, while the red show the layer lattice matched to rutile (110) where there is 0.14% stretch strain along [100] and 0.84% stretch strain along [010]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

rutile (110) surface, three structural variations of rutile (110) surface (neutral, negatively-charged and oxygen-deficient) combining with graphene monolayer are considered, respectively. In all of these cases, the graphene monolayer is located about 2.0 Å away from the rutile (110) surface and all atoms are allowed to fully relax. For neutral graphene/rutile (110) composites, relaxed graphene sheets move away from the rutile (110) surface so that the nearest distance between a carbon atom and the surface O atom is 2.86 Å (as illustrated in Fig. 2). There is no evidence of bending deformation for graphene layer. However, the shortest interspace of graphene sheet and rutile (110) surface is 2.69 Å in composite with oxygen deficiency, and the graphene sheet becomes to be buckling. The binding energy of the graphene and neutral rutile (110) surface is only 0.514 eV, and this binding energy is so weak that it hardly changes geometrical structure of graphene. And two types C–C bond length (1.41 Å and 1.44 Å) are found in graphene/rutile (110) composites, corresponding to the values found in previous reports [28,29]. The work function of three composite systems are estimated, and the theoretical values are 4.06 (neutral), 3.45 (negatively-charged), and 3.25 eV (oxygen-deficient), respectively. Generally, work function can be used to measure the ability of losing electron in materials. Because the negatively-charged and oxygen-deficient composites donate additional electrons more easily than neutral one does, their work functions are smaller than that of neutral composite. The work function of TiO_2 is influenced by its surface structure and polarity, which is also consistent with previous reports [30,31].

3.2. Charge populations analyses of graphene/rutile (110) composites

The atomic charges and bond populations of three composites are calculated and shown in Table 1. Mulliken charges are determined to be -0.01 to $-0.02e$ for carbon atoms of graphene, -0.59 to $-0.70e$ for oxygen atoms, and 1.30 – $1.36e$ for titanium atoms. In negatively-charged composite, Mulliken charges of carbon are from -0.02 to $-0.04e$, and in oxygen-deficient composite, the charges of carbon change from -0.03 to $-0.06e$. Remarkably, there are excess charges both in negative-charged and oxygen-deficient rutile (110) surface, and the charges of oxygen and titanium atoms hardly change in comparison with those of oxygen and titanium atoms in neutral surface. But the charge populations of graphene in three composites are different. Therefore, it is sug-

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