Effects of the electric field on the properties of ZnO–graphene composites: a density functional theory study

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In this work, the effects of the electric field on the properties of ZnO–graphene composites were theoretically studied using density functional theory calculations. Three types of ZnO–graphene composites including composites of pristine graphene, graphene with defects as well as graphene oxide and a ZnO bilayer were studied. We calculated and analyzed the binding energies, charge transfer, band structures and work functions of the above composites under the external electric fields. The DFT calculation results demonstrate that the binding energies are sensitive to the electric field, and increasing the external electric field gives rise to stronger binding energies. The extent of charge transfer is correlated with the magnitude of the external electric field, but the band gaps are hardly affected by the external electric field. The work functions vary depending on the different structures of the composites and surface sides, and they are also tunable by the external electric field.

1. Introduction

Transparent conducting films (TCFs) have been widely used in consumer electronics such as flat-panel displays, touch screens, as well as solar cells for energy conversion. The industry standard TCF is tin-doped indium oxide (ITO), which usually demonstrates a resistivity of the order of $10^{-4}$ cm. However, there are some significant drawbacks of ITO, such as its high cost due to the scarcity of indium, instability in hydrogen plasma, poor mechanical properties, and use of toxic etching solution. Therefore, looking for new materials that can replace ITO is imperative. Zinc oxide, which is much less expensive than indium oxide, has been increasingly studied as an alternative to ITO thin film as an electron transport layer. Compared to ITO, ZnO exhibits numerous characteristics that may enable its efficient use in the above devices. ZnO is an n-type semiconductor with a wide band gap of 3.37 eV. However, for application in electrical devices, improved electrical properties of ZnO thin films are still required. Graphene has also been widely considered to be next-generation TCF since its discovery in 2004 because of its unique two-dimensional structure, remarkable electrical mobility, optical transparency to visible and near-infrared light as well as excellent mechanical properties. The applications of graphene with consisting of only the carbon element for integration into devices with multifunctionality are still limited by its intrinsic properties. In this regard, the hybridization of different types of materials is crucial as it can enable versatile and tailor-made properties with performances far beyond those of the individual materials. Hybrid heterostructures of the ZnO semiconductor or nanostructures with two-dimensional (2-D) graphene layers are emerging as new materials for fabricating transferable and flexible optoelectronic and electronic devices. Incorporation of graphene into the ZnO thin film increased the carrier mobility with optical transmittance unaffected, and it is easy to etch. The ZnO–graphene hybrid composites showed good electrical conductance and optical transparency, comparable to that of a homogeneous graphene layer, as well as ultraviolet and visible light emissions inherited from the ZnO nanorods. Shin et al. fabricated graphene cathode-based BHJ OSCs with a power conversion efficiency (PCE) of 1.55% using the MPCVD-grown ZnO thin film as an electron transport layer. From these experimental efforts, it has been recognized that the ZnO–graphene nanocomposites offered improved performance compared to individual components due to the synergistic effects caused by the interfacial interaction. We have studied the polarized surface of ZnO interacting with graphene, nevertheless, the atomic details at the interface of graphene and ZnO under an external electric field remain poorly understood. It is common and effective to use an external electric field to modulate the corresponding physical properties of graphene. The carrier concentration in a semiconductor device could vary due to the electric field effect and, consequently,
electric current was changed. Therefore, it is argued that the ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. On the other hand, compared with other approaches, the electric field is clean, easily acquirable, and adjustable in both direction and intensity, which impart it with many advantages. It is currently an important issue to make clear the effect of an external electric field on the electronic properties of the composites and develop more electronic applications. We believe this issue is important and valuable to be intensively studied by theoretical studies. First-principle calculations based density functional theory can fundamentally extend our ability to understand the relation between the external electric field and electronic properties at atomic-scale resolution.

Herein, we reported DFT calculations to characterize the interface between graphene and the ZnO surface under an external electric field. The aim of the present study is to establish a basic physical picture of nanocomposites by interconnecting ZnO with graphene and to study the relation between the interface structure and properties under an external electric field. In order to reflect the nuances of the structure, we employed three representative structures, which we have used to investigate the interaction between graphene and the TiO2 employed three representative structures, which we have used to investigate the interaction between graphene and the TiO2 cluster, including pristine graphene (P-G), graphene with monovacancy (V-G) and graphene with epoxy (O-G). The influences of the direction and size of the electric field on the properties of the composites were studied. We calculated the properties as functions of the electric field for the composites of graphene on a ZnO bilayer. Firstly, the configurations and total binding energies of ZnO-graphene composites were calculated. Then the charge transfers were also calculated to study the electronic properties of the composites. Finally, the calculation results proved that the composites with different interface structures could have tunable work functions.

2. Computational details

The DFT calculations were performed by applying Dmol3 program in Materials Studio 5.5 package of Accelrys Ltd. The generalized gradient approximation (GGA) with the Perdew, Burke, Ernzerhof (PBE) exchange–correlation functional was used to treat all electronic energies of exchange correlation. A double-numeric quality basis set with the polarization functions (DNP) was employed, which was comparable with the Gaussian 6-31G** basis set in size and quality. The TNP basis set was tested for the P-G system, and the difference in energy was within 2%. The core electrons were treated using DFT semicore pseudopotentials (DSPPs). A thermal smearing of 0.005 Ha and an orbital cut-off of 5.8 Å were used to improve the computational performance. The convergence criteria for the geometric optimization and energy calculation were set as follows: (a) an energy tolerance of $1.0 \times 10^{-7}$ Ha, (b) a maximum force tolerance of 0.002 Ha Å$^{-1}$, and (c) a maximum displacement tolerance of 0.005 Å. Because the weak interactions are not well described using the standard PBE functional, an empirical dispersion-corrected density functional theory (DFT-D) approach proposed by Grimme$^{28,29}$ was adopted. The long-range dispersion, van der Waals (vdW) interaction, was described using a damped interatomic potential. The total energy was

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$

$E_{\text{KS-DFT}}$ is the self-consistent Kohn–Sham energy and $E_{\text{disp}}$ is the dispersion correction and is described by

$$E_{\text{disp}} = -\frac{1}{6} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{C_{ij}^d}{R_{ij}^6} f_{\text{dmp}} (R_{ij})$$

where $N$ is the number of atoms, $s_b$ is the global scaling factor specific for the exchange–correlation functional used in the DFT calculations, $C_{ij}^d$ is the dispersion coefficient between any atom pair $i$ and $j$ at distance $R$, $f_{\text{dmp}}$ is the damping function, which avoids near-singularities for small $R$.

The initial structure of graphene and ZnO bulk were derived from Materials Studio 5.5 package. We cut two ZnO double layers along the (0001) direction of bulk wurtzite and allowed atoms and cells to fully relax to describe the ZnO layers. Then, a $4 \times 4$ single graphene layer containing 32 carbon atoms was used to match the $3 \times 3$ stoichiometric ZnO layer. The lattice mismatch of the graphene and ZnO was 1.62%, which was small and the structure was stable. Vacuum space at Z axes was 15 Å to avoid the interaction between the periodic images. For graphene on ZnO layers, atoms and cells were fully relaxed.

The binding energies of the composites were calculated by using the expression:

$$E_b = E_{\text{total}} - E_G - E_{\text{ZnO}}$$

where the $E_{\text{total}}$, $E_G$ and $E_{\text{ZnO}}$ denote the total energy of the ZnO–graphene system, isolated graphene and ZnO, respectively. A negative $E_b$ corresponds to a stable adsorption structure.

3. Results and discussion

In this work, three structures, pristine graphene (P-G), graphene with monovacancy (V-G) and graphene with epoxy (O-G), were used to represent the graphene and graphene with vacancy and epoxide groups. For ZnO, a bilayer ZnO sheet was employed. A previous DFT study$^{30,31}$ predicted that ZnO ultrathin films and monolayer sheets preferred a graphitic structure. Later, Tusche et al.$^{32}$ successfully synthesized the bilayer-thick ZnO(0001) films, which confirmed the theoretical predictions. The structure of the ZnO bilayer ultrathin films was derived from the optimized two ZnO double layers of bulk wurtzite. In our calculation results, the distance between the two ZnO layers was 2.47 Å, and the interlayer Zn–O bond was 1.92 Å, these agreed well with the previously reported results.$^{33}$ We also considered the effects of an external electric field perpendicular to the ZnO/graphene interface in the range of $-0.3$ to 0.3 V Å$^{-1}$. A positive value means the electric field is from graphene to ZnO, and a negative value means the electric field is from ZnO to graphene.
3.1. Geometric structures and binding energies

For V-G and O-G, the positions of epoxy and vacancy were located at different initial states including hollow sites, top of O and Zn sites. After full relaxation, the optimized configurations of three ZnO–graphene composites without an external electric field are shown in Fig. 1. The influences of an external applied electric field on structures were relatively weak and negligible. For ZnO–P-G, the interlayer distance between the ZnO and P-G layers was 3.10 Å, which was slightly shorter than the interlayer distance of graphite. This distance indicated that the interaction between ZnO and P-G layers was relatively weak and vdW interaction. There was no structural distortion observed for graphene and ZnO compared to the isolated components. For ZnO–V-G, after full relaxation, the graphene and ZnO layers moved relatively, the almost same situation was found for the vacancy initially at a hollow site and at the top of the Zn site. The distance of C1–Zn1 was 2.11 Å, indicating chemical bond formation between the C atom and the Zn atom. Meanwhile, the ZnO layers distorted obviously and strongly reconstructed. The Zn1 atom was pulled closer to the graphene layer, however, the O atom coupled with Zn1 in the second layer was pushed outward and out-of-plane. The distances of the other Zn–O couples were also changed. However, for the vacancy at the top of O, after full relaxation, optimized structures were similar to those shown in Fig. 1a; there was no chemical bond formation between graphene and ZnO layers, and no distortion was observed for the ZnO layer, the binding energies were 0.39 eV lower than that in Fig. 1b. In the case of ZnO–O-G, no matter the initial state at the hollow site, top of O or Zn sites, after full relaxation, the optimized structures were almost the same as shown in Fig. 1c and the binding energies changed no more than 0.05 eV. The interaction between the ZnO and O-G induced distortion in ZnO. Some of the Zn atoms in the first layer moved toward graphene and the O atoms in the second layer moved outward. The distances of O1–C1, O1–C2, O1–Zn1 were 1.47, 1.48, 2.46 Å respectively. The distance of O1–Zn1 was longer than the typical Zn–O bond in wurtzite but shorter than the vdW distance. The stable structure of zinc oxide was wurtzite structure, namely, zinc and oxygen atoms were four coordinated. In the ultrathin film, ZnO was reconstructed to form graphene-like structure, which was three coordinated. When the ZnO dimonolayer was close to epoxy or vacancy graphene, the dangling bond or epoxy interacted with the zinc atom. The zinc atom was restored to a four coordinated structure and the surrounding atoms also induced deformation. The calculated binding energies using the external electric field are shown in Fig. 2. Regardless of the presence of an external electric field, the binding energies were in the order of ZnO–V-G > ZnO–P-G > ZnO–O-G. The ZnO–V-G system showed the highest binding energy among these three systems, compared to the vdW interaction between the ZnO layer and C atoms, the existence of a strong C–Zn bond enhanced the overall energy. For ZnO–O-G, the epoxy O atom was closer to the ZnO layer, however, C atoms were pushed far away from the ZnO layer, and this led to the decrease of the overall vdW interaction. For ZnO–P-G, the lowest binding energy corresponded to the field-free state with a value of −2.35 eV. The binding energy increased as the electric field increased no matter positively or negatively. For ZnO–V-G and ZnO–O-G systems, the lowest binding energies were found for the 0.1 V Å⁻¹ electric field. The corresponding binding energies were −2.69 and −2.18 eV respectively, which were slightly lower than that of electric field-free values of −2.70 and −2.19 eV. The binding energy increased as the electric field increased at a positive electric field larger than 0.1 V Å⁻¹. The binding energies increased more sharply under a negative electric field. Fig. 2 gave the fact that the binding energies were sensitive to the electric field. By calculation of Mulliken charge population, we found charge transfer between graphene and ZnO layers, and the charge transfer of every C atom was not uniform. The C atoms close to O atoms showed positive charges, but those atoms close to Zn atoms showed negative charges. Therefore, the Coulomb interaction was responsible for the mainly electrostatic interaction between the graphene and ZnO layers. The charge transfer was determined by the magnitude of...
electric fields. Electrostatic interaction could be increased distinctly with the electric fields as shown in Fig. 2. Here, comparison of $E_b$ between DFT and DFT-D levels was discussed, and it was found that the differences were obvious. The $E_b$ values of ZnO–V-G, ZnO–P-G and ZnO–O-G systems were −2.70, −2.35 and −2.19 for the DFT-D level, and −0.64, −0.38 and −0.26 for pure DFT.

3.2. Charge density and charge transfer
In order to investigate the bonding character and charge transfer at the composite interface, we studied the electronic total charge density and Mulliken charge population. The electronic total charge density slices for the composites were shown in Fig. 3. As shown in Fig. 3a and c, there was no electron orbital overlap between the ZnO layer and P-G or O-G. In contrast, the electronic charge plot was partly overlapped between V-G and ZnO layers (Fig. 3b), leading to more orbital mixing and indicating the formation of chemical bonds.

The C1 atom neighboring the vacancy had a sp$^2$ dangling bond due to the single carbon vacancy. When the Zn atoms of ZnO were closer to the C1 atom with the dangling bond, the C1 atom was apt to form a chemical bond with Zn atoms. This agreed well with the binding energy results.

To understand the charge transfer quantitatively, we calculated the Mulliken charge populations. The charge transfer of graphene, corresponding to the total sum of the Mulliken charge populations of the C atoms (for ZnO–O-G include the epoxy O atom) under an external electric field, is shown in Fig. 4. A positive value meant the charge transfer occurred from graphene to ZnO, in contrast, charge transfer from ZnO to graphene showed a negative value.

For all systems, graphene showed negative charge when an external electric field was absent. In other words, charge was apt to transfer from ZnO to graphene. From positive to negative, the populations order was ZnO–V-G, ZnO–P-G, ZnO–O-G with the charge transfer values of −0.082, −0.011, −0.113 respectively. The V-G with a dangling bond preferred to donate electrons, therefore, the Mulliken charge population was more positive or less negative. The O-G with a larger electronegative epoxy O atom accumulated charge on the epoxy O atom, and showed negative charge instead. The charge population was more negative as the electric field became more positive, indicating that the layer facing the electric field would accumulate charges. However, the layer facing away from the electric field would undergo charge depletion. The relative order of charge populations was retained. The overall charge transfer was small, for instance, the charge transfer of ZnO–P-G under a 0.3 V Å$^{-1}$ electric field was −0.19; thus, per C atom the charge transfer was only −0.006.

3.3. Band structure and work function
In order to investigate the influence of an external electric field on the electronic structure of composites, we calculated the band structures of the composites. The band structures of the three composites under −0.3, 0 and 0.3 V Å$^{-1}$ external electric fields are shown in Fig. 5. Fig. 6 shows the band gap as a function of the external electric field. We could see from the band structure that as the external electric field varied from negative to positive, the valence band shifted upward relative to the Fermi level for all the composites. The band gap of ZnO–P-G was located at the $K$ point of the Brillouin zone; however, it was too small to be seen for the band structure.

![Fig. 3](image-url) Electronic total charge density slices of (a) ZnO–P-G, (b) ZnO–V-G, (c) ZnO–O-G.

![Fig. 4](image-url) Charge transfers of composites under the external electric fields.
vicinity of the defect. There was a considerable band gap between the valence band and the conduction band. Band gaps deviated from the $K$ point, and lay between $G$ and $K$. According to Amara et al., there were flat bands in the localized states on the graphene with vacancy. Compared to these results, the two bands were separated from each other, this could be because of the interaction between graphene and ZnO. For ZnO–O-G, in analogy with the monovacancy, a distinct band gap and flat band were observed. These were similar to the case reported by Amara et al., in which an extra C was on the bridge site of the graphene. The main differences were that there was a small downward peak for the flat band in our results, which might arise from the interaction between graphene and ZnO, and the O atoms at the bridge site. For all the systems, in spite of the slightly upward shift of the valence band, the electronic band maintained the structures under the external electric field. The band gaps of the composites were in the order of ZnO–O-G > ZnO–V-G > ZnO–P-G. The band gap was slightly decreased as the external electric field became positive, however, the differences were quite small, within the range of $-0.3$ to $0.3$ V Å$^{-1}$, the change in the band gap was less than 0.05 eV. Therefore, when the composite was applied in an electronic device, the conductivity was hardly affected by the external electric field. It is noted that the DFT method usually underestimates the band gap of semiconductors due to the self-interaction error, so the actual band gap of composites should be larger than the calculated values. However, the relative order and trend were credible. The band structures showed that the valence band and the conduction band shifted upward or downward simultaneously under the electric fields, so the band gaps were hardly affected by the electric fields.

Work function (WF), which is defined as the difference between the Fermi level and vacuum level, is an important electronic property for evaluating the photoelectric effect and field emission properties of a surface. The WFs of the composites as functions of the external electric field are shown in Fig. 7. The WF of ZnO side was higher than that of graphene side without an external electric field. We could see that the WF of ZnO side of ZnO–V-G was 5.51 eV, which corresponded to that of ITO. The WFs of ZnO sides were in the order of ZnO–V-G > ZnO–O-G > ZnO–P-G, and the graphene sides were in the order of ZnO–V-G > ZnO–P-G > ZnO–O-G. When a positive electric field was applied, the WFs of graphene sides decreased while those of the ZnO side increased. The WFs showed a contrary behavior upon the application of a negative external electric field. In other words, the side facing the electric field showed increased WF, and the side lying with its back to the electric field showed decreased WF. It is feasible to obtain a desirable WF through a change in interface structure and different sides, for instance, select the ZnO side of ZnO–V-G with the demand of high WF and select the graphene side of ZnO–O-G with the demand of low WF.

4. Conclusions

In summary, we have performed density functional calculations to study the interface structures and properties of graphene on ZnO layers under the external electric fields. Three types of structures, P-G, V-G and O-G were employed to represent the
graphene surface with defect and graphene oxide. The geometric structures and binding energy results showed that the graphene interaction with ZnO occurs by vdW interaction, and results in the formation of a stable film structure. The composites are stable under the external electric field. The O atom on graphene leads to lower binding energy and conductivity. The composite becomes more stable but decreases conductivity in the case of C vacancy. A stronger external electric field (both positive and negative) gives rise to stronger $E_{\text{gap}}$. The effects of an external electric field on conductivity were negligible. The WFs were tunable properties with different constructions under an external electric field. ZnO and graphene composites formed TCFs with tunable properties for electronic devices. Our results give a further insight into the interface of composites and properties at an atomic level. We suggest future experiments to give more attention to the ZnO–graphene nanocomposites and examine their potential as TCFs.

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**References**


